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Difficulties in

Printing Acetate Crepes

By T. C. HUTCHINS

THE first process of importance in the printing of any color is the preparation of the printing paste. Before the dyestuff can be applied to the fabric with any degree of success it must first of all be brought into as soluble a state as possible. If complete solubility is impossible then the finest possible state of dispersion is aimed at by the color-mixer, previous to application. From this point of view dyestuffs may be divided into two classes (1) those which are applied to the fabric in a state of solution and (2) those which are applied in a finely dispersed condition. In the first class we find such colors as the acids, basics, chrome mordant, indigosol and direct dyestuffs. In the latter or second class are found most of the vat dyestuffs and the type of dyestuff generally used for printing on acetate rayon fabrics. There is a wide variety of different brands in this class. Some of these brands are supplied in powder form, some as pastes. If the former, then the dyestuff has to be acted upon by special dispersing agents in order to bring it into a finely divided condition for printing. If the paste type of dyestuff is used then the difficulty of dispersion is practically overcome from the beginning, so far as the printing is concerned. Powder colors for printing have certain advantages in respect of storage and stability, but the writer is of the opinion that the use of the paste forms is decidedly advantageous from many points of view. Some of these advantages may be enumerated as follows: (1) The pastes are ground very fine before leaving the works and are therefore in the best possible state of dispersion for printing. (2) More level prints are produced as a rule, especially in dark shades. (3) The very fine dispersion may also result in some cases in better fixation. (4) As a result of better fixation the washing off properties are improved and there is less risk of unfixed dyestuff bleeding into white grounds.

Perhaps a practical illustration will help to make this matter clear. In making practical trials of Acetate colors for printing the writer used certain members of a well known brand of this class of dyestuffs, in powder form. A number of the colors gave excellent results by using a dispersing agent for pasting the powder color. Several however did not, and the manufacturers agreed to supply them in paste form. The result was that the colors that had formerly given poor results in powder form now gave excellent prints in the paste form. The conclusions are obvious.

The matter of thickening must receive careful consideration especially if the prints are to be produced by the screen method of printing. Gums of one kind and another are recommended for use along with the type of color under discussion. In this connection the natural gums are widely used, largely in consequence of their clarity and solubility. Some of the gums do not give very high color yields and as this is important from the economic point of view it is necessary to give a good deal of attention to this aspect of production. For screen printing, gum tragacanth probably gives better all round satisfaction than any other thickening agent. It not only gives good color value but is easily removed from the fabric after printing by washing in cold water only, in addition to this, prints produced by its use are very well penetrated. It should also be recognized that a thickening may play a part in the dispersion of the color on the fabric. In support of this contention the writer remembers using several thickenings as a test along with one particular color. The more viscous of the printing pastes gave specky results and gum tragacanth gave a perfect result with the same color. A good deal however depends upon the type of printing process and class of dyestuffs involved, so that it is not possible to lay down any hard and fast rules for the use of any one thickening or mixtures thereof.

In the actual preparation of the print color great care should be taken when using powder brands, to ensure the thorough pasting of the dyestuff before adding the diluted paste to the thickening. Perhaps in this connection it

should be emphasized that the absorption of color by the acetate fiber is not comparable to the same phenomenon in other fibers. The acetate fabric being itself a colloidal body, has under certain conditions, the faculty of absorbing other similar bodies. The type of dyestuff used is in a colloidal state and the actual state that exists between the color and the fiber when printed or dyed may be described as a solid colloidal solution of the dye. From this it will be gathered that it is of the utmost importance to have the color in the finest possible state of division or dispersion before being applied to the fabric.

As our discussion concerns crepe fabrics it should be noted that the degree and type of crepeing have very definite results on the production of the prints. Most crepes for printing are also dulled during the crepeing process and this process of dulling must be very carefully carried out if regular results are to be expected. Crepeing is usually carried out in such a manner that the fabric in the open width has its whole surface exposed to the action of the liquor. If for any reason, one part of the fabric is better processed than another then the print colors will have a different effect on this area of the cloth. It is well known that the duller the fabric the better the absorption of the dyestuff and it follows that the better the absorption the less risk there will be of the colors bleeding in the final washing-off process. Not only is this the case but the goods are not so liable to the fault of sublimation during steaming. If matt crepes are to be printed therefore, the point to bear in mind is, the duller the fabric the better result so far as printing is concerned.

The objection may be raised that the duller the fabric the more difficult it will be to print from the penetration point of view. If the goods are not processed right there is something to be said for this objection in that there is a real risk of the formation of soap precipitates in the fabric. The crepeing and dulling process involves the use of large quantities of soap and under certain unfavorable conditions familiar to all processors the precipitation of insoluble soaps is a common difficulty. If this should occur during crepeing, then most certainly the cloth will show resist marks when printed. The remedy is obvious when it is remembered that there are many excellent sulfonated fatty alcohols on the market.

If the color and the cloth are in proper condition for printing, by the screen method, a perfect print should be produced by one stroke or at the most two, one forward and one back, of the rubber squeegee used by the printer. If more pressure than this is necessary there is something wrong with either color or fabric or both. If the color does not penetrate for any reason, the result will generally be that too much print paste is left on the face of the cloth, in an effort to obtain a perfectly penetrated print. The effect of this will be seen on washing-off the goods. At this stage the unfixed color will wash-off into the becks and if there is a large excess, general staining of the white grounds will result. From this it will be seen that the choice of a proper thickening in order to get good penetration of the color, and a thoroughly clean fabric on which to work, are matters of the utmost importance.

In order to avoid staining of white grounds attention to the following points is recommended: (1) Thorough dulling of the material. (2) As long a time as possible in the steamer. (3) The minimum of color on the face of the cloth. (4) The use of a thickening that will penetrate thoroughly. (5) Thorough washing of the prints in a copious supply of cold water.

With regard to the delustering of the acetate silk, it has already been made clear that the better delustering has been carried out the better the absorption of the print paste. Steaming presents one or two difficulties where delustered fabrics have to be dealt with. The usual recommendation for full development of the print colors is twenty minutes steaming without pressure. If a festoon steamer is used, this time will produce satisfactory results but if the goods have to be steamed in a cottage steamer other arrangements will have to be made. In a cottage steamer the goods are wound on to reels and transferred from thence to poles which with their burdens of cloth are then hung on iron frameworks and pushed into the body of the steamer and steamed for the requisite period. In order to keep the folds of the material from touching in the steamer and marking-off as a result, the printed pieces are wound on with a back-grey. This interposes the thickness of the grey between each fold of print thus rendering marking-off impossible.

The result of using greys is that the goods have to be steamed for much longer periods in order to develop the colors. There are two principal dangers to be avoided: (1) Re-lustering of an already de-lustered fabric as the result of too much pressure or too long a period of steaming. (2) Sublimation of the prints either in the form of a mark-off or springing and bleeding of the colors. If the cloth is really well delustered there is little danger of a re-luster. The best way to avoid such a contingency, however, is to use as little pressure as possible or none at all. The sublimation difficulty may be overcome in a similar manner and if better fixation of the colors is desired at any time, the prolongation of the steaming period without pressure will produce the desired result. As a matter of fact, the longer the steaming period the better (within limits) from the points of view of fixation and cleanliness in washing-off.

The next point for consideration is that of the amount of print color on the cloth. Theoretically this should always be the minimum that will produce a good printing impression. If, however, there is difficulty in penetration, the printer is forced to use a great deal more color than is necessary. The only satisfactory cure for this trouble is prevention of precipitates during crepeing as indicated in a previous paragraph. Lastly, good penetration of the prints and thorough washing-off in the final stages are mentioned as necessary to clean white grounds in prints of this type. In the first instance suggestions have already been made as to thickenings but

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Principles of

Dyeing with Basic Dyes*

By L. R. PARKS and P. G. BARTLETT

BASIC dyes have been defined by Parks and Beard[10] as organic color bases which contain the color in the basic radical, dissociate in water to give colored cations, form true aqueous solutions, and are removed by the fiber as the color base. According to this definition dyeing with dye bases should be analogous to the adsorption of inorganic bases by charcoal.

As a general rule dye bases are so insoluble in water that they are not suitable for dyeing purposes. However, their salts are in general use. These come into the market usually as the chlorides, although sometimes the acetate, oxalate, sulfate, or even the nitrate may be found. These salts hydrolyze in water according to the reaction

$$RA + H_2O \rightleftarrows ROH + HA$$

where R represents a monovalent cation of the dye and A the monovalent anion.

The concentration of ROH may be regulated by controlling the hydrogen ion concentration of the solution. Thus, the concentration of ROH may be increased by the addition of hydroxyl ions which neutralize the HA formed and thus allow the reaction to proceed to the right. Hydroxyl ions may be supplied by the addition of alkali hydroxides or of salts which hydrolyze basic.

It is known that hydroxyl ions are very strongly adsorbed, and that the adsorption of sodium hydroxide or potassium hydroxide by charcoal may be increased by either increasing the hydroxyl ion concentration or by the addition of a salt with a common ion.

It is the purpose of this paper to show that the behavior of dye bases towards adsorbents is similar to the behavior of sodium hydroxide or potassium hydroxide towards charcoal.

EXPERIMENTAL PROCEDURE AND RESULTS

A. *The Effect of Inorganic Salts on the Adsorption of Inorganic Bases.*

The methods used in this work were similar to those used by Parks and Bartlett[7] in their work with acid dyes. Activated sugar charcoal was used as the adsorbent, and phenol red as the indicator. Phenol red is extremely sensitive to carbon dioxide, consequently the solutions were all boiled before and during titrations. When dealing with alkaline solutions it is particularly necessary to boil the solution after each addition of the acid in order to determine the true end point.

To determine the effect of electrolytes on the adsorption of inorganic bases, the amount of base was kept constant at 0.01 N. and the amount of electrolytes added was varied. The solutions were prepared by taking 50 cc. of 0.1000 N. base and mixing it with a definite amount of salt solution in a 500 cc. graduated flask and diluting to volume. This method gave solutions of the desired neutral salt concentration and were 0.0100 N. with respect to the base present. Before treating with charcoal, these solutions were titrated with 0.0100 N. standard acid solution, using phenol red as an indicator, as an assurance that the prepared solutions were 0.0100 N.

From each solution two 125 cc. portions were taken. Each portion was shaken with 1.2500 grams of charcoal in a 500 cc. Erlenmeyer flask. The flasks were placed in a constant temperature bath and kept at 25 degrees C. for 24 hours. The charcoal was then removed by filtering. Fifty cc. portions were titrated again with 0.0100 N. standard acid. The difference in concentration before and after treatment with charcoal indicated the amount adsorbed.

The results are tabulated in Table I and shown graphically in Figure 1. The values (x/m) are stated in milligram equivalents of base adsorbed per gram of charcoal.

TABLE I

Adsorption of 0.01 N. Sodium Hydroxide and 0.01 N. Potassium Hydroxide in the Presence of Increasing Concentrations of Their Chlorides

Sodium Hydroxide		*Potassium Hydroxide*	
NaCl.N	x/m	KCl.N	x/m
0.00	0.5787	0.00	0.6030
.10	.6920		
.20	.7128	.20	.7258
.30	.7341		
.50	.7407	.50	.7682
.75	.7485		
1.00	.7581	1.00	.7800
1.50	.7700	1.50	.7911
2.50	.7885	2.50	.7957
3.50	.7967		
		4.50	.8050

The amount of sodium hydroxide adsorbed increases rapidly with increased concentration of sodium chloride up to about 1 N. concentration of added salt. With more

*Contributed from the Pond Chemical Laboratories of the Pennsylvania State College.

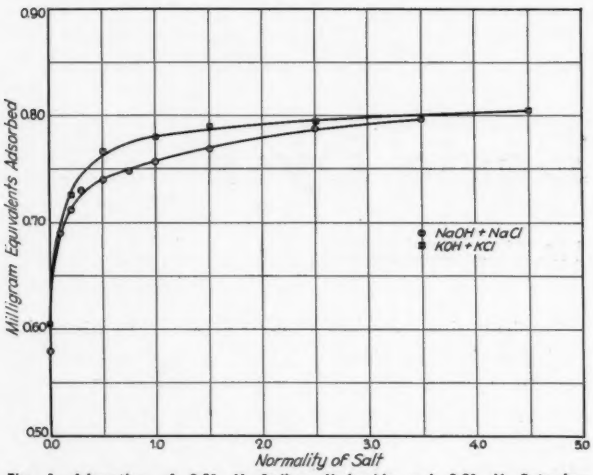


Fig. 1—Adsorption of 0.01 N Sodium Hydroxide and 0.01 N Potassium Hydroxide in the Presence of Increasing Concentrations of their Chlorides.

concentrated solutions in respect to salt, the increase in adsorption of the base approaches a linear function of the increased salt concentration.

The presence of potassium chloride affects the adsorption of potassium hydroxide in a similar manner. Potassium hydroxide is adsorbed to a greater extent than sodium hydroxide.

B. *The Effect of Inorganic Salts on the Adsorption of Dye Bases.*

Activated sugar charcoal and unbleached, thoroughly washed wool were used as adsorbents. Methylene Blue Base was chosen as a typical, difficultly soluble, dye base. This was prepared by the hydrolysis of Methylene Blue.

The concentration of Methylene Blue Base was regulated very carefully in order not to cause precipitation of the dye in the dye bath. To determine the effect of electrolytes in the dye bath, the amount of Methylene Blue was kept constant in each solution and the amount of electrolyte added was varied. The solution and wool mixtures were boiled under reflux condensers for forty-five minutes, the wool was then removed immediately from the solution, the remaining solution cooled, and aliquot portions titrated with titanium chloride. Experiments in which charcoal was the adsorbent were carried out in a similar manner. Exactly two grams of charcoal were mixed with 250 cc. of solution and held just under the boiling point for forty-five minutes, and filtered while hot. Approximately the first thirty cc.'s of filtrate were discarded to allow for the removal of some of the dye by the filter paper. Titrations were performed as before.

Aliquot portions of the original solutions, not mixed with adsorbent, were also titrated. Thus it is possible to determine the original concentration of the dye bath, the concentration of the dye in the bath after dyeing, and by difference, the amount of dye removed by the adsorbent.

Experiments with Technical Methylene Blue.—The total volume of each dye bath was 250 cc., which contained 75 mgs. of Methylene Blue and a certain number of cc.'s of tenth normal electrolyte. The amount of electrolyte was varied for each sample. Each sample of wool weighed approximately two grams.

Sodium phosphate, sodium tetra-borate, and sodium sulfate cause a marked increase in the amount of Methylene Blue Base adsorbed. Hydrochloric acid decreases the amount of Methylene Blue adsorbed.

With zero salt concentration the adsorbent takes up only Methylene Blue (the hydrochloride). However, if a salt which hydrolyzes basic is added to the dye bath the adsorbent takes up Methylene Blue Base and some Methylene Blue. As the amount of Methylene Blue Base increases, the amount of Methylene Blue approaches nearer and nearer to zero.

Since there is no reliable method of determining the amount of Methylene Blue and Methylene Blue Base adsorbed for each increase in the concentration of added salt, the mgs. of dye adsorbed per gram of adsorbent are reported in mgs. of Methylene Blue.

The effect of varying concentrations of electrolytes are shown in Table II.

TABLE II

The Effect of Hydrochloric Acid and Salts Which Hydrolyze Basic on the Adsorption of Methylene Blue Base

(*75 mgs. of dye to 250 cc. of solution*)

Adsorbent	cc. of Salt 0.1 N	*Mgs. of Dye Adsorbed Per Gram of Adsorbent in the Presence Of:* Na_3PO_4	$Na_2B_4O_7$	Na_2SO_4	HCl
Wool	0.00	13.39	13.39	13.39	13.39
	1.50	17.72	18.50	14.45	7.35
	3.00	21.90	21.07	14.82	3.45
	8.00	33.50	29.35	16.47	0.99
Charcoal	0.00	27.64	27.64	27.64	27.64
	1.50	30.70	31.52	30.00	26.45
	3.00	33.65	34.12	31.20	24.77
	8.00	35.35	35.35	32.00	24.57

Experiments with Purified Methylene Blue.—Methylene Blue was obtained in a pure state by repeated crystallization of a high grade of commercial "concentrate". The water used in the crystallizations and dyeing process was distilled from a Barnstead still and gave a pH value of 5.8. This is in agreement with the work of previous investigators[1, 3, 4] who have shown that pure distilled water in normal equilibrium with the CO_2 of the atmosphere has a pH value of 5.6 to 5.8 depending on the source of the water supply and atmospheric conditions.

All pH determinations were made with the stick antimony electrode[8, 9]. In order to reach air equilibrium the dye bath solutions were cooled in a CO_2-free atmosphere and then tumbled for one hour.

The volume of each dye bath was 250 cc., which contained 40 mgs. of purified Methylene Blue and a certain number of cc.'s of 0.025 N. sodium hydroxide. Each sample of wool weighed approximately four and a half grams.

The effect of varying concentrations of sodium hydroxide are shown in Table III. The mgs. of dye adsorbed per gram of wool are reported as mgs. of Methylene Blue.

TABLE III

Effect of Added NaOH to Dye Bath of Methylene Blue

(*40 mgs. of dye to 250 cc. of solution, Wool as the adsorbent*)

cc. added NaOH (0.025N)	pH before dyeing	pH after dyeing	Adsorbed per gm adsorbent
0.00	4.06	4.75	4.28 mgs.
1.00	4.52	4.95	4.39
2.00	4.86	4.95	4.54
3.00	7.45	4.94	4.79
4.00	7.97	5.12	5.08
5.00	8.26	5.25	5.25

DISCUSSION AND INTERPRETATION OF RESULTS

Inorganic Bases.—Activated carbon contains spaces of all sizes and shapes between the carbon atoms. Some of these spaces are too small to hold one hydroxyl ion, while others are large enough to hold one but not two, etc. If now sodium hydroxide is added to activated carbon the hydroxyl ion is more strongly adsorbed than the sodium ion. The sodium ion tends to diffuse to portions of the solution where its concentration is not as great as at the surface of the carbon. Thus there is a tendency to pull the adsorbed hydroxyl ion away from its attendant carbon particle. The adsorption of sodium hydroxide by activated carbon may be expressed by

(1) $\boxed{C} + NaOH = \boxed{C}\ OHNa$

where $\boxed{C}$ represents an activated carbon particle regardless of size. The ionization of $\boxed{C}$ OHNa may be represented by

(2) $\boxed{C}\ OHNa \rightleftarrows \boxed{C}\ OH^- + Na^+$

The complex $\boxed{C}\ OH^-$ has the properties of a complex ion having one or more valences (depending on the number of adsorbed hydroxyl ions) and differs from a complex ion only in regard to size.

There is a stage in the adsorption of sodium hydroxide where it is impossible to remove all of the adsorbed base from the adsorbent by washing with water. This has been pointed out by Parks and Keller[11] in their description of the difficulty with which part of the adsorbed base is removed from cotton by washing with pure water. This stage, in the case of charcoal, may be pictured as the part of the hydroxyl ions which are surrounded on nearly all sides by carbon atoms. If these hydroxyl ions cannot be removed by washing the cations must also remain in the charcoal or in close proximity to it.

Now if sodium chloride is added to a solution of sodium hydroxide the excess of sodium ions in the solution will decrease the tendency of the sodium ions, of the adsorbed sodium hydroxide, to diffuse away from the carbon particle. Therefore reaction (2) is written reversibly. This allows the hydroxyl ions adsorbed to become more firmly attached to the carbon, by penetrating further into the spaces between the carbon atoms. This penetration leaves more room for more hydroxyl ions to be adsorbed, although less firmly, at places nearer the surface of the carbon particle.

In this investigation it was found that 0.01 N. sodium hydroxide solutions remained cloudy in appearance after filtering. Evidently the charcoal was peptized by the sodium hydroxide to form a colloidal dispersion. However, when solid sodium chloride was added to this cloudy filtrate, the dispersed charcoal rapidly settled out, and was easily filtered. The excess of sodium ions decreases the ionization of the adsorbed sodium hydroxide to a point where precipitation occurs. The adsorbed sodium hydroxide remains on the particles of carbon when they are precipitated. This is shown by the fact that removing the charcoal decreases the alkalinity of the solution. On this basis the charcoal particles should be dispersed again when the precipitating agent, sodium chloride, is removed by washing, because of the renewed dissociation of the adsorbed sodium hydroxide. This is indeed the case.

The adsorption of potassium hydroxide in the presence of potassium chloride is similar to the case of sodium hydroxide from solutions containing sodium chloride. The fact that potassium hydroxide is more strongly adsorbed than sodium hydroxide shows that the potassium ion is more strongly attracted to the charcoal than the sodium ion.

It is well known that more base is adsorbed per gram of adsorbent if the hydroxyl ion concentration of the solution is increased. The quantitative adsorption of dissolved bases in relation to the end concentration is expressed by the equation

$$x = a.C^{1/n}$$

where x is the amount adsorbed by one gram of the adsorbent material, C is the equilibrium concentration of the solution after adsorption, a and n are constants depending on the nature of the base and the adsorbent. The value of the exponent (1/n) is less than one.

Basic Dyes.—The basic character of dye bases is due to the presence of hydroxyl groups within the molecule which ionize basic in aqueous solutions. Basic dyes may be represented by the general formula ROH where R is a monovalent colored cation and OH is the hydroxyl anion. Since basic dyes form true solutions in water, the ionization of ROH may be expressed by

$$ROH \rightleftarrows R^+ + OH^-$$

There may be all degrees of solubility of dye bases. Some may be very soluble in water, others less soluble, and some practically insoluble. If the dye bases are soluble in water they may be used, as the base, in the dye bath. However, if they are so insoluble that they are not suitable for dyeing purposes, then their water soluble salts may be used. The colloidal principles in every case are analogous to the adsorption of sodium hydroxide by charcoal. Only the soluble and slightly soluble cases will be considered here.

Soluble Dye Bases.—If the dye base is soluble in water it may be added, as the base, directly to the dye bath. In this case the amount of dye adsorbed by the adsorbent may be increased by increasing the concentration of the dye in the solution. This follows from the expression

$$x = a.C^{1/n}$$

for the adsorption isotherm. On the other hand the amount of dye base adsorbed may be increased by increasing the concentration of either the color cation or the hydroxyl ion. It is much more economical and convenient to control the hydroxyl ion concentration and thus regulate the amount of color cation taken up by the adsorbent. If the hydroxyl ion concentration is increased by the addition of alkali hydroxides or salts which hydrolyze basic, then more dye base will be adsorbed, and if the hydroxyl ion concentration is decreased by the addition of acids, then less dye base will be adsorbed.

Insoluble Dye Bases.—As a general rule dye bases are so insoluble in water that they are not suitable for dyeing purposes. Their salts, such as the chlorides, oxalates, sulfates, and nitrates are soluble and may be used in the dye bath. They should be called Salt Dyes, when they are used for dyeing purposes without the aid of alkali hydroxides or of salts which hydrolyze basic.

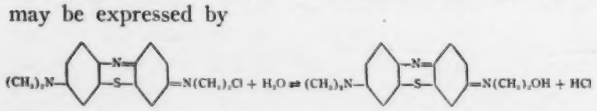
Miller[6] states: "When activated, ash-free sugar charcoal that has adsorbed a known amount of methylene blue is suspended in sodium hydroxide solution, the sodium hydroxide is neutralized and there appears in solution an amount of sodium chloride equivalent to the chlorine originally held by the charcoal. No trace of color, however, is imparted to the solution by this treatment. At room temperature it requires a considerable length of time with shaking or a number of extractions with N/50 sodium hydroxide to remove all the chlorine from the charcoal. Boiling for a few minutes seems to remove it completely."

This, of course, means that Methylene Blue Base is at least as strongly adsorbed as Methylene Blue. It is a fact, as will be shown later, that the dye base is much more strongly adsorbed than the dye hydrochloride.

Miller's experiments suggest that an insoluble dye base may be applied to an adsorbent by first dyeing with a water soluble salt of an organic color base and then treating the dyed material with sodium hydroxide or a salt which hydrolyzes basic. However, such a procedure is not practical.

If a suspension of Methylene Blue Base is placed in a dialyzer the dyestuff will slowly dissolve and pass through the semi-permeable membrane. This shows that it forms true aqueous solutions.

A solution of Methylene Blue containing 40 mgs. of dye in a total volume of 250 cc.'s has a pH value of 4.06. This corresponds to 17.4 per cent hydrolysis as calculated according to the method of Denham[2]. The hydrolysis may be expressed by



The concentration of the Methylene Blue Base may be regulated by controlling the hydrogen ion concentration and thus the hydroxyl ion concentration of the solution. The concentration of the dye base may be increased by the addition of hydroxyl ions which neutralize the hydrochloric acid formed and thus allow the reaction to proceed towards the right. Hydroxyl ions may be supplied by the addition of sodium hydroxide or salts which hydrolyze basic.

When 4.6730 grams of wool are dyed in a solution containing 40 mgs. of Methylene Blue in 250 cc. of solution, 20 mgs. of dye remain in the dye bath. The pH of the dye bath changes from 4.06 before dyeing to 4.75 after dyeing. A fresh solution of Methylene Blue which contains 20 mgs. of dye in 250 cc. has a pH value of 4.75.

This indicates, then, that with zero sodium hydroxide concentration wool adsorbs only the hydrochloride from an aqueous solution of Methylene Blue and not Methylene Blue Base.

Examination of Table III shows that the pH of the dye bath, before dyeing, increases with increased concentration of sodium hydroxide. However, the pH after dyeing increases very slightly. This indicates that the hydroxyl ions are very highly adsorbed. As the hydroxyl ion concentration of the dye bath is increased, the hydroxyl ions adsorbed penetrate further into the spaces between the wool molecules. This penetration leaves more room for more hydroxyl ions to be adsorbed, although less firmly, at places nearer the surface. The adsorbed hydroxyl ions carry with them their attendant dye cations, and thus increase the amount of Methylene Blue Base taken up. As the amount of Methylene Blue Base increases, the amount of Methylene Blue (the hydrochloride) approaches nearer and nearer to zero. Since there is no reliable method of determining the amount of Methylene Blue Base and Methylene Blue adsorbed for each increase in concentration of sodium hydroxide, the mgs. of dye adsorbed per gram of wool were reported as mgs. of Methylene Blue.

If too much sodium hydroxide is added to the dye bath the concentration of the hydroxyl ions will become so great that the solubility product of Methylene Blue Base will be exceeded and a precipitate will form. The maximum amount of sodium hydroxide which may be added to Methylene Blue without causing precipitation of the base, is therefore dependent upon the concentration of the dye cation in the dye bath. There was no evidence of precipitation at a pH of 8 and a dye concentration of 40 mgs. per 250 cc.

It is well known that sodium phosphate and sodium tetra-borate hydrolyze basic in aqueous solutions. Kraus[5] has shown that a boiling solution of sodium sulfate reacts basic. These salts, therefore, will increase the amount of Methylene Blue Base adsorbed from solutions of Methylene Blue. Furthermore, an examination of the data of Table II shows that the salts with the greater degree of

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Fifteen Years of

Hosiery Dyeing—II

By NOEL D. WHITE

(*Continued from September 9th issue*)

A MAKESHIFT LABORATORY

MY NEW employer had promised to put up a laboratory for me later, so I tried to make the best of the kerosene oil stove and my dime enameled pot for the time being. Only a dyer who ever used a kerosene oil stove to dye a sample on it will know the predicament I was in. Besides having to watch the burners, to prevent smoke entering the pot and the eyes of the operator, I had to watch the evaporation of the bath, to avoid toasting the samples. This having occurred a couple of times, while I was busy on something else, I gave the stove my blessing and decided to provide a hot water bath without delay.

There was a round wooden tub in the dyehouse to keep boiling water handy when needed for any purpose. That would do for me. I drove a hole in the handle of a dipper and a nail in the top of the tub. When filled to the brim with boiling water I could set the dipper on it, mooring it to the edge of the tub. It worked quite well. No more smoke in my eyes and no more toasted samples. What did I care if people giggled seeing me working on my unorthodox laboratory? For beakers I used pint milk bottles (keeping them out of sight to prevent trouble with the milk man), I dissolved and kept my dyestuffs on trial, or to make samples with, and never stopped using them until the end. My Kodak graduate served quite well until I got the proper equipment a long time after.

The first color given me to match was a dark shade of navy. My employer had written me about that shade and on my way South I stopped in the New York offices of several dyestuff dealers I knew, as I already mentioned, to make inquiries about the best dyes to use for dyeing hosiery but particularly for that shade of blue and to bring some product samples along with me.

During my visits to these offices I was agreeably surprised to find one man who really cared that I should make good, even to the point of advising me to use some dyes made and sold by competing concerns. I was to be reminded of this fact as being the more remarkable by the attitude of another man, who offered to help me in my first trial of matching that shade of blue, he proved that instead he wanted to make sure that no other dyes than those he sold should enter our dyehouse. His attitude proved a boomerang to him and his firm. I had found a blue dye that was giving the desired bloom to that shade of blue, but this man wanted me to discard it in favor of the several dyestuffs of his that it took to get only nearer to the same result! He was trying to convince me that it was better to use two or three cotton dyes to get the same result I could get from a single one because he did not have one similar to the one I had found. It convinced me that I would have to keep on the lookout, as I did while in my last position, keep on watching for every dye that was being developed by the new, domestic dye industry. I decided to get for this work what I thought was best, not from hearsay or salesmen talk, but only after I convinced myself from trials and investigation and regardless of by whom or where it was made, whether it was a soap, a chemical or a dyestuff. This policy, strictly adhered to, proved to be the main cog to keep our progress in high gear.

Every chemical, every dye that was brought to our attention had a chance to prove its worth to us. To gain entrance in our dyehouse and a place on the shelves in our stock room a dye was challenged like a juror in an important trial. We gave it several tests in the laboratory and if found promising we tried it for its leveling quality on a batch or two in the dyehouse. When adopted its permanence with us was assured until another dye was found that proved to be superior. That is the only way to keep abreast with the progress of the industry.

BUILDING UP CONFIDENCE

In accordance with the mill's policy they had sent to their dyestuff dealer a sample of the shade of blue they wanted. It was to be called Night Blue. They had also sent a sample of that shade to several other dealers with orders to match it and send 10 pounds of the mixed dye along with their match, but it had to be exact. Their idea was to select and buy the ready mixed dye from the firm that had made the best match, a kind of contest for a masterpiece.

That had been done before my arrival and I did not know about it until some time later when the returns started to come in. I was kept busy testing the products as they arrived, matched material and 10-pound cans of dyes, each one worse than the one preceding it. They were anxious to put in line that shade because it was

gaining in popularity very fast just then, but everyone of the mixtures received proved more or less disappointing. By that time with the samples of dyes I had collected and brought along from New York I had dyed a blue that came up to their expectation. I dumped all those 10-pound cans in a keg, mixed them up thoroughly and disposed of the whole lot by adding a small dose of it with every lot of Night Blue I dyed.

I had assured the manager that I was fully capable and willing to match any shade he cared to put in line and I thought I had gained enough confidence to let me work out the matching problem from now on. One morning I was surprised to find on my desk a ten-pound can of dyestuff labeled: S. & C. Grey, No. 157, and a ten-pound can labeled S. & C. Palm Beach, No. 304. They had been sent by their regular dyestuff dealer. My first impulse was to ship both cans back, but decided to await development so I cleared them off my desk and tried to forget about it.

When the superintendent finally came in he announced that they had decided to put in a shade of Grey and a Palm Beach. They had ordered them matched and "this is what we want, I will send down the goods directly." He gave me a package containing two pieces of knitted goods with a tag attached to each and a letter with instructions how to prepare the bath, the percentage of dye to use and how much salt.

I did not like the idea and told him so. I said that since I had charge of the dyehouse matching and deciding what dyestuffs to use was a part of that charge. That my idea of running a dyehouse was to do it without interference and I was going to see about it. While I was talking I could see in his face that he resented my show of independence, but said nothing except to mumble while he was leaving that he was going to see about it too.

A LINE ON SUPERINTENDENTS

This was our first clash. I could see that I had to assert myself now or to be dictated to forever by this man. The first impression I had of him was proving correct. His actions had already convinced me that his job was bigger than he was. I was to learn, as time went on, that he was even worse than I thought at first. His idea of being a good superintendent was not only to rule with an iron hand, but to subjugate to his will and make abject slaves of everyone working for him. If we could not work together for the best interest of the mill they could look for another dyer. I was going to run the dyehouse without being obliged to "yes sir" him or anybody else. This was the time to act.

Maybe the reason I felt so daring was that I had received a letter from the superintendent of the mill I had left so recently. He had written me that he had taken charge of the dyehouse and hoped I would go back and work with him. In order to understand this situation it must be explained that, while I was working in that mill in Massachusetts, this man had made it plain that I had to assume full charge of the dyeing and the entire responsibility thereof. That he wanted nothing to do with it and I had to answer for my charge directly to the agent of the company, who also acted as sales manager. We had always been in the best of terms and quite friendly. As my successors had not been giving satisfaction he had offered to take charge of the dyehouse and wanted me back to run it for him. I had been spoiled by eight years of undisputed freedom, under those conditions and was now chafing under the restraint I saw coming. I was quite willing to go back. If these people wanted me to stay here they would have to let me run the dyehouse as I had done in my last place. The work I had done so far had been quite satisfactory and I felt very confident. What I did not know was how easy it was to fool me and how much can be accomplished by using diplomacy to subdue a rebellious spirit.

When I submitted my grievance to the manager he knew about it already. He was prepared for it and what he had to say was the result of careful thought. Very suavely he took the blame for the occurrence and said that it was not the superintendent's doing, but that he thought he was making it easier for me. If I objected to it I could send those dyes back. He added, however, that he would appreciate it if I would try to use those mixtures, that they had been prepared purposely for him, that he was anxious to put those two shades in line and while I was using them I could get my own formulas for them to be used in the future. If that was the way I felt about it, it was all right with him, as a matter of fact he agreed with me and there would be no further interference. I felt he was covering up his superintendent and I frankly told him what I thought.

This man had inspired in me the utmost confidence. I really liked him and in his presence felt free to speak my mind with sincerity. So I told him my aim was to please, my only ambition was to see the mill grow and myself to grow with it. I was going to use those two cans of dyestuff and do the best I could with them. By the time I got back to the dyehouse I felt like a whipped cur, for I realized I had lost the first round and made an enemy of the superintendent. I had dared to question his authority and now he would surely teach me a lesson in subordination. Well it could not be helped now, I would make the best of it here and give up the idea of going back to Massachusetts.

PREPARED DYE MIXTURES ON TRIAL

Now I had a chance to verify my contention that, when dyeing with ready mixed dyes, results could not possibly be as good as when the dyer did his own mixing. In prewar time on many occasions I had received circulars from dyestuff dealers asking me to send to them our dyeing troubles, let them match our samples, but had always considered the practice detrimental to the dyers' brotherhood. If these dealers could solve all the dyeing troubles for our employers what could prevent them from entrusting their dyeing to their firemen, for instance, or to any unskilled laborer and throw us out of our jobs?

Not being in sympathy with such a practice maybe it was prejudice on my part that made me dispise the use of dyestuff dealers' laboratory and their ready mixed dyes. Since I had a couple of them on hand I would be glad to put them to the test. There may be some good in them after all. (I believe this last thought was the reaction induced by my recent defeat.)

The formulas for the two shades read thus:

100 *Pounds Polo Grey*

S. & C. Grey 157..... 4 ozs.
Salt ..... 5 lbs.
Boil one hour, wash, finish.

100 *Pounds Palm Beach*

S. & C. Palm Beach, 304..... 4 ozs.
Salt ..... 5 lbs.
Boil one hour, wash, finish.

Very simple if correct, so I thought. It did not prove so easy as that though. To finish a presentable job I had to make some additions and when I got the shades they wanted the formulas read somewhat differently:

100 *Pounds Polo Grey*

S. & C. Grey 157..... 4 ozs.
Direct Orange ..... 4 grs.
Neutral Grey .....10 grs.
Silk Orange ..... 5 grs.
Fast Red ..... 3 grs.
Glauber Salt ..... 5 lbs.

100 *Pounds Palm Beach*

S. & C. Palm Beach..... 4 ozs.
Direct Yellow ..... 5 grs.
Fast Red ..... 4 grs.
Azo Yellow ..... 4 grs.
Glauber Salt ..... 5 lbs.

It will be noticed that there was no acid used in these shades and that may be the reason I had to use the silk colors to correct the matches. If salt had been used, as set down in the original formulas, it is quite possible that the result would have been nearer to the samples, but salt is harmful to the silk fiber, makes it harsh, brittle and it impairs its luster. It also rushes the color on both fibers making it hard to control and to level the shade.

The Palm Beach shade did not sell as anticipated, but the grey proved to be quite popular. I was glad to be kept busy on that shade because it could be dyed in a shorter time than any of the other colors we had and turn out more production with the scant equipment we had as yet. My supply of the grey mixtures was getting low and I was still undecided what to do. I was using a prepared mixture for the Cordovan and with the slight change made in the formula had eliminated all troubles. With the little additions we had set down on the formula for the grey it was now working quite well. I was inclined to let well enough alone and send in an order for 25 pounds of S. & C. Grey 157. Was I getting lax and inclined to follow the line of least resistance? I did. Laxity won and the order was sent on its way.

THE DEATH BLOW TO MIXED DYES

When the 25 pounds of S. & C. Grey 157 arrived it was stored away until needed. It should have been tested, but laziness and an inconvenient laboratory made me neglect that important duty, but it taught me another lesson and I was surely learning fast in those days.

As soon as the 10-pound can was empty the 25-pound can was opened and a batch dyed with the new shipment of grey. We had taken for granted that the mixture was the same, the formula with addition was followed to the letter. When a stocking was taken out, to look at the match, what we saw will remain in our memory until Gabriel will blow the horn and I am sure St. Peter will forgive me for what I thought and said on that occasion. I hope now that the mixer of that grey did not have to go to the places I committed him that day.

I took the stocking and the sample to the superintendent, then I brought it to the manager to show him how reliable ready mixed dyes could be, then I went back to think over what could be done to correct that ruined shade. At that time there was not much use for strippers in the dyehouse. Dyers did not resort to strip and restrip in order to get results. The strippers I knew I would have ordered if I had ever thought of such a contingency. Anyway, after I had cooled down and could think rationally I proceeded to correct that match. The color was all uneven, the cotton was several shades too red, and the silk off on another slant. I soaped the batch for about one hour at 180° F., then rinsed it. This reduced most of the color from the silk. In a new bath with 3 pounds of acetic acid, at the boil the color on the cotton was stripped quite considerably. I washed the lot, whizzed it and straightened out the tangles in the bagged goods. Then I made a new start and built up the grey shade in a fresh, neutral bath.

In the meantime the superintendent had sent for his friend, the dyestuff salesman. I had kept the stocking to show him what the new shipment of grey had produced. He was sorry about it. So is the crocodile who, they say, sheds tears after he has eaten his man on the bank of the Nile. "What you should do," he added, "is to send us your samples to match and, instead of mixing the dyes for you, we will send you the formulas with the names of the dyes and the percentage of each to be used, like we do for the dyers around here." I told him that if he sent me the names of the dyestuffs and the amount of each used in the mixture we had on hand it would be greatly appreciated. As far as matching our samples for us it was quite unnecessary, I considered it a part of my job, I was able and willing to do it myself. When his help was needed we would indeed be glad to take advantage of the facilities offered by his concern, and if he appreciated my goodwill, he should never try to impose any of his mixture in this mill. This last was intended for the benefit of the superintendent and I noticed it had gone home.

When the formulas and contents of the dye mixtures

we had finally were sent to me, I found out that in all cases we had to pay for a lot of common salt at the price of dyestuff, which at that time was quite high. It was put down in the formulas as "binder" and was needed to bring up the volume to the right percentage, so I was told, and in some cases it amounted to fully one-third of the total. When I showed this item to the manager he readily agreed that the saving was worth the expense of a better laboratory than the one I had rigged up.

A WORTHWHILE RESOLUTION

Contrary to expectation the outcome of all this was not going to improve my good standing with the superintendent. He could see that I was gaining in the estimation of our employer and his authority over the dyehouse was slipping. He did not like that. He was determined to hold on to it with the mistaken idea that he could break my spirit and subject me to his will like the rest of his subordinates. Like them I was supposed to tremble in my boots and quicken my movements at his approach. Most of all I disliked the patronizing attitude he had assumed towards me, but I was determined to make the best and try to get along the best I could.

He was crafty, but I felt his dislike for me growing. However, he had the sense to recognize the value of what I had accomplished so far and even if he had not openly praised my work he knew I was a valuable addition to the organization. He could do me no harm if I kept up the good work. Upon my good work depended the prosperity of the mill, so I resolved to consider his attitude towards me as a blessing. It would spur me on to achievements, it would make me quit the line of least resistance, never be satisfied with good enough work or let well enough alone. My work should always be the very best obtainable, regardless of handicaps, even in spite of them and I was going to prove to my employer that his confidence in me was justified.

(To be concluded in next issue)

Acetate Crepes—

(Continued from page 528)

as a useful addition to the print paste the writer would recommend some of the well known brands of dispersing and levelling agents for this purpose. Besides assisting penetration, these products in many instances give much leveller prints by reason of their dispersing capabilities. This is particularly the case with the type of dyestuffs mentioned in the course of this article as the fixation of these colors depends entirely on their dispersive properties.

With regard to washing-off prints of this type, the process should be carried out in a copious supply of running water if possible, in slack washing machines. The main difficulty in washing is to keep the excess of color which is washed off along with the thickening, from being dyed on to the unprinted portions of the material. The remedies for this are: (1) To keep the printed material moving swiftly in the rope form through the wash water. (2) To use a plentiful supply of water running during washing. (3) The use of a small percentage of sulfonated fatty alcohol along with the wash water. The washing is, of course, carried out in the cold, and with regard to the addition of sulfonated alcohol this will need to be renewed at intervals until the prints are clean. The addition of such products, however, need only be resorted to when very dark colors are involved, light prints and colors will wash off perfectly well with cold water only.

When thoroughly free of surplus color the prints may be suction dried or even lightly extracted in a hydro, before being stentered for finishing. As a final word of advice it should be emphasized that the washing-off process should not on any account be hurried. A little extra time spent at this stage in the careful removal of all surplus thickening and dyestuff will well repay itself in a much enhanced finished article.

Basic Dyes—

(Continued from page 532)

hydrolysis have the greater assisting effect on the adsorption of dye bases.

Hydrochloric acid decreases the amount of Methylene Blue adsorbed by either wool or charcoal. This is because the hydrogen ions of the hydrochloric acid are so strongly adsorbed that they tend to displace the less strongly adsorbed color cations of the Methylene Blue.

SUMMARY

Dyeing with basic dyes is an adsorption phenomenon analogous in every respect to the adsorption of inorganic bases by charcoal. Basic dyes are organic color bases which contain the color in the basic radical, dissociate in water to give colored cations, form true aqueous solutions, and are taken up by the fiber as color bases. The amount of dye base adsorbed is dependent on the hydrogen ion concentration of the dye bath.

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PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

SEPTEMBER 23, 1935

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TECHNICAL PROGRAM FOR THE ANNUAL MEETING AT CHATTANOOGA DEC. 6-7

(*Reprinted from last issue*)

In accordance with the custom followed by other technical and scientific societies, the Program Committee of the American Association of Textile Chemists and Colorists invites any member of the Association with a worthwhile message in the field of textile chemistry to present a technical paper at the Annual Meeting in Chattanooga, December 6 and 7. This paper will then be published later in the Proceedings in the AMERICAN DYESTUFF REPORTER.

Authors of papers are asked to submit titles as soon as possible to the Chairman of the Technical Program Committee. In order to encourage more intelligent discussion, abstracts of all papers will be published in advance of the meeting. These abstracts must be in the hands of the Program Committee before November 1. Final complete copies of the papers ready for publication in the Proceedings must be submitted at the time of presentation of the paper.

There has always been criticism from some sources that too few practical mill men take part in our Annual Meetings. Mill Men! Here is an opportunity for you to silence these critics by presenting papers which will steal the show from the laboratories of the dyestuff, chemical, and machinery manufacturers.

CARL Z. DRAVES,
Chairman, Committee for Technical Program,
273 Converse Street, Longmeadow, Mass.

Remarks*

By Jos F. X. Harold

I WOULD like to pay tribute to a member of the organization who has passed away but who has never received full credit for what he did on pine oil. I refer to Charles E. Kaltenbach, whom some of you may remember.

It is true that as far back as 1908 and 1910 there was a good deal of experimentation done in Charleston on the use of pine oil as a textile aid in the kier, but it never amounted to anything practical.

At the time when Kaltenbach did his work on the introduction—I think he can be credited with that—of pine oil into the textile trade, pine oil was used as a detergent by autoists and repairmen, that is, in the form of this gel—that last thing that was passed around. That was the use to which it was limited—cleaning grime off the hands.

The work of Kaltenbach and Stephens in Newark showed that it was a wonderful silk-degumming agent, that it could be used in reduced amount, as compared with soap, and that it left the silk with a better hand and feel, and that even some of the sericine could be left in, without any impairment of the softness properties which, of course, meant a gain in the net weight of the silk.

Mr. Kaltenbach also applied it to kier-boiling in a large way in a number of textile mills, notably the Taubel Hosiery Mill at Riverside, New Jersey. The Zavon Company, were then making this jelly for the use of autoists. These products took a new lease on life and many went into the production of this pine-oil jelly which had quite a vogue from about 1926 on. They used a 1, 3, 5 ratio—1 of oil, 3 of soap, and 5 of water. And as you know, especially you men engaged in the soluble oil industry, any new way of marketing water is a distinct improvement in the textile art. (Laughter.)

Kaltenbach's contribution to this industry has been neglected and as he was one of our prominent charter members I think it ought to be remembered in his favor.

The use of this pine oil has grown by leaps and bounds since and the use of pine oil emulsions in the dyeing of acetate yarns and acetate fabrics in general is under one of the Kaltenbach patents. Pine oil also seems to be extremely useful as a dispersing agent for the less soluble colors. It seems to impart a property to a dyestuff to work outside of its class; that is, it will make insoluble dyes work as soluble ones, and vice versa.

It has made it possible even to dye silk with the sulfur dyes without the slightest damage, so that one can use these comparatively cheap dyes to substitute the high-priced silk dyes.

*Delivered at meeting, N. Y. Section, March 1, 1935, following a paper on Pine Oil presented at that meeting by Harry E. Smith which will be published at a later date.

The field has been very crowded from the patent standpoint. Ellis has a patent for the use of solid pine oil soap. Billy Van, you know, sells his pine oil soap that is supposed to breathe the perfume of the pine forest. (Laughter.) But Kaltenbach, our fellow-member, was the first one to make a solid oil pine soap with up to fifty per cent of pine oil, whereas these pine oil soaps that you buy in the drug store only have just a few per cent, for scent purposes.

There were some other members of our organization who went into the manufacture of these pine oil jellies who have made small fortunes.

The chief advantage of it, I think, rests in the fact that it isn't an oil at all, but that it does something to a fiber that none of the other things do, and that is largely on the basis of the fact that it is one of the cheapest aromatic alcohols we can have. Terpineol, as Dr. Smith well drew attention to, is the main element in the article and I think the virtues of the pine oil emulsion are to be attributed to the peculiar solvent effects of the alcoholic constituents in the substance, rather than its oil value. It is really improperly called an oil. Most people think that pine oil is something like turpentine; that is, that it is either a hydrocarbon of the turpentine type or it is an oil. Strictly speaking, it isn't that at all.

There is an immense future for it in other lines of chemistry. For example, it is a wonderful perfume base and I think a great deal of its progress in the future will be along that line, if perfumes can be made any cheaper or sold any higher. (Laughter.)

Etched Lace

I welcomed Mr. Zisman's suggestion, and this is the start of it. I stressed it with him, however, when he asked me to speak, that I was not to be featured in any way, and I find that I have been more than featured. That is, the device of silence was changed to a device of secrecy, which is quite a different thing, and I am quite sure a great many of you of the sportsmanlike type, men who no matter how old they are have young ideas, came here under the impression that perhaps a pink elephant was to be exhibited or other such entertainment arranged. I am sorry to disappoint those younger-minded members of the organization and to tell you that my topic is not to be included under the scope of entertainment. I am going to talk, following Mr. Zisman's suggestion, on a topic that has what might be termed in the reporter's language to have "news value." I am going to talk on "etched lace."

The art is rather old and has its implications in arts that were in existence long before our Patent Office was started. It derives from the fact that in any textile aggregate composed of two or more unlike materials the one may be removed from the other by a proper choice of chemical.

For example, we all know how to take wool and cotton apart. There are two general methods. You may dissolve the wool in caustic soda—every tailor even knows that (laughter)—or you may take the mixed fabric and treat it with an acid, oxalic acid, sulfuric acid, or any acidic chemical like aluminum chloride—and then by the after-treatment you carbonize the cotton. You take all the water, as it were, out of the cotton and leave nothing but carbon, which is left with so little strength that it can acually be dusted away from the residual wool. This is called the operation of carbonizing—a dry method of removal.

The use of caustic soda might be said to be the wet method of removal of animal fiber from a vegetable fiber.

In this wet removal of one fiber from another, we have what might be called the implications of these etched fabrics and the methods by which they are made. Patents covering them may be said, then, to date back to those patents and devices by which cotton is removed from wool, or wool from cotton.

In addition to the purely analytical wet method of separating one fiber from another, there are methods that are used for determining the pattern or appearance of the final product.

For example, you can take a fabric, a cotton fabric, and weave wool threads into it here and there in a patterned way. You can then throw that fabric into caustic soda. Your wool fibers are dissolved out and you have a patterned effect.

There is a purely analytical method of separating cotton and wool, used as a means of making a textile residual which shall have a pattern or especially desired effect. That method had been used in the 80's for securing effects in wool and cotton mixtures. By that method, even on a common loom, products could be made that resembled Leno weaves and the more complicated Jacquard designs to some extent.

As the synthetic rayon products grew, this method of arriving at a textile pattern by the wet etching out of one of the constituents began to be applied to the synthetic rayons of the soluble type. It is not generally known that nitrocellulose is not only soluble in organic solvents, but is also soluble in caustic soda. The weaving of nitrate fibers or yarns, then, into an aggregate of cotton could lead to a patterned effect afterwards by the etching out of the nitrocellulose either in an organic solvent or in caustic soda.

The use of nitrate and cellulose acetate led to even newer devices and the treatment of new complexes, for here we were dealing with the possibility of taking a solubilized thread, to be afterwards etched out in the presence of an animal fiber, and separating it from the untreated animal fiber, which could not be done before by the previous caustic soda treatment. That is, in those methods where caustic soda was used as a separant, or to produce by solution of one fiber a residual, we had been limited in the past to residual cellulosic fibers. With the use of nitrate and acetate of cellulose, we had a new form of residual possible. That is, by the use of an organic solvent the residual could now be wool or silk, which it couldn't be before.

So we had a vast extension in what might be called the "wet etching art," when the acetates and the nitrates came into play, especially with the acetates, because they were regarded as the only safe cellulosic esters to leave in a textile fabric, the nitrates being rather dangerous.

Modern methods, however, in certain lines of the etched lace industry have made it possible to actually use nitrate of cellulose as such in fiber form as a safe textile element. Such an element may be made safe, at least until it is discharged, by a wet etching process, by endowing the cellulose nitrate with zinc chloride, magnesium chloride, and any other ignifuge, as it is called, or fireproofing agent that may be desired.

Fabrics can be woven either with cellulose acetate in them or cellulose nitrate in them, and the design can then be made in the final fabric by the use of caustic soda in the case of cellulose nitrate, dissolving the cellulose nitrates or organic solvents which dissolve either the nitrate or acetate of cellulose.

An interesting trade in this method of acting on nitrate of cellulose has been built up in what is called the lace etching method. Here in the etched lace method a nitrated cellulose is used as a background for the stitching of a cotton lace. The trade prevails chiefly around Union City here. A large number of companies make the lace that way. A cellulose nitrate background made safe by endowing it with zinc chloride—made temporarily safe—is used. The cotton lace is stitched upon it and then the whole multiple fabric or plied fabric, consisting of an upper face of cotton and a background of cellulose nitrate, is thrown into a caustic soda bath, the background of cellulose nitrate being completely dissolved and the lace riding free.

This has been developed within the last ten years—the use of cellulose nitrate as a safe etched lace background.

Remarks*

By H. C. Chapin

I AM fortunate in being with you tonight, because the dates of the Council and Section meetings coincide. I wish that it might occur more often.

Most notable perhaps at our meeting this afternoon was the addition of forty-seven members to our roll.

*Presented at meeting, N. Y. Section, March 1, 1935.

This is I think the fourth consecutive Council meeting, beginning with the one held in October, at which we have elected forty or more members. So the Association is growing quite rapidly.

I want to congratulate you again on the splendid meeting here at which the New York Section was the host, and particularly I want to thank Mr. Kennedy and Mr. Winnell, at the Registration Desk, for the work which they did so quietly and so perfectly. It was particularly helpful to the Secretary.

The next meeting as you all know will be in Chattanooga, the first Friday and Saturday of December. We have had a very hearty welcome from that Section, in fact from all of the Southern Sections, and I hope many of us will be able to go down together. (Applause.)

SUB-COMMITTEE ON MERCERIZING

THROUGH the appointment of Sidney Edelstein as a Research Associate of the A.A.T.C.C. to work under the supervision of the Sub-Committee on Mercerizing of which Prof. Charles B. Ordway is Chairman, the work of this committee passes into a more active stage.

Since it is authoritatively estimated that the Chattanooga district produces between one-fourth and one-fifth of the United States' entire output of mercerized yarn, it is quite fitting that the experimental work should be conducted at the University of Chattanooga. The University authorities and the Chemistry Department of the Institution are cooperating to the fullest extent and have not only provided working quarters for Mr. Edelstein, but have also made an appropriation to cover necessary additional equipment.

Mr. Edelstein graduated from the Massachusetts Institute of Technology in 1932 and since that time has had three years experience in research and plant work at the Dixie Mercerizing Company in Chattanooga. For this reason he should be well qualified to carry on this work.

ANNUAL OUTING, SOUTH CENTRAL SECTION

THE summer outing of the South Central Section was held on Signal Mountain on August 2nd and 3rd. With members of the Southeastern and Piedmont Section as guests about 170 were registered for the two days.

Many handsome prizes were awarded to the winners of the various contests—golf, bridge, swimming and shuffle board. In the golf tournament prizes were awarded as follows: *low gross*—Frank M. Wood; *2nd low gross*—T. W. Piper; *low net*—Nestor Grotelueschen; *2d low net*—Richard P. Smith; *3rd low net*—Fletcher Kibler; *high score*—R. H. Evans; *blind bogey*—Homer Whelchel.

Saturday morning was devoted to sightseeing, which was followed by dinner and dancing in the Hangar Saturday night.

Respectfully submitted,

H. B. KIMBRELL,
Secretary.

CALENDAR OF COMING EVENTS

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Meeting, New York Section, Elm Golf Club, Paterson, N. J., Friday evening, October 4th.

* * *

Annual Meeting, Chattanooga, Tenn., December 6th and 7th.

AMERICAN
DYESTUFF
REPORTER

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NEXT YEAR'S VACATION

INASMUCH as most of us who were lucky enough to have a vacation (we are not referring to the popular (?) "payless furlough") have probably returned to work by now, we think it an excellent time to bring up the subject of next year's vacation although many may think we are a little previous in our choice of subject for discussion. After we have explained what we have in mind you will see reason for the choice.

One of our friends who is engaged in the business of selling to the wet processing branch of the textile industry has brought to our attention the fact that the present system of taking vacations does not work out very advantageously for those persons who are engaged in peddling their wares to the textile mills. You will also see that it is not very convenient for the mill man either. As it stands now, the buyer (dyer, finisher, chemist, bleacher, owner, etc.), in one mill will take his vacation at one time and the buyers in the other mills in the same locality will take theirs at entirely different times. Thus if a salesman ordinarily makes ten calls in one town and during his regular visit he finds that three of the mill men he wishes to see are away on vacation he is able to make only 70% of the calls that he would ordinarily make. In order to see the three men who were away on his regular visit he will have to make an additional trip to that town and he finds that it costs him just as much to make the second trip as it did the first. To carry this further if each of the ten mill men took his vacation at a different period it would necessitate ten different trips if the salesman wished to see all of them. To make the situation more complicated the salesman also wishes to take a vacation. While he is doing this one of his customers finds that he needs to reorder certain items or he may need the advice of the salesman in some particular matter. A salesman from a competing firm drops in and takes the order or is able to solve the difficulty of the mill man. The net results of the present system are greater expenses and loss of sales for the travelling man and inconvenience to the mill man.

Having brought up the subject we should accordingly offer a solution to the problem and we could suggest that the yearly rest period for persons engaged in selling to the mills and buying for the mills be abolished. However we won't make this suggestion because it is impractical and furthermore we believe vacations are of value; so instead we will again listen to the friend mentioned previously who, as well as making the criticism, has also a solution to offer:—

"The solution to this problem is relatively simple—providing proper cooperation is forthcoming. Why not have a universal vacation period for all mill men—say the first two weeks in July? It stands to reason that the absence of one or two men a week all during the summer will hamper the efficiency of any industry during the entire period, whereas if the industry shut down for two weeks such inefficiency would not result. The plan has been tried in individual plants with success. Of course it would not prove to be equally successful if all mills, or a majority of the mills, would not agree. With such a plan in effect the salesmen selling to the mills would naturally take their vacations at the same time, secure in the knowledge that they were not losing business or favor to some competitor.

"If a sufficient number of mills would agree to this plan it would force the others to follow suit because the idea would follow through in those industries which supply the mills and those which take the products of the mills. Many mills have a period in the summer when they are shut down anyway so why not all agree to shut down for a certain predetermined period? There are many mill men, overseers, superintendents, etc., who are so situated that they do not have regular vacation periods; they are able to take only a day or two now and then. Such a plan as I have described would surely meet with their approval. However it is to the mill owners that such a plan must be presented in the hope that they will see enough merit in the idea to make it universally acceptable. Anyway, I would like to get the opinion of the mill owners as well as the other people who are selling to the mills."

We also should like to know what the mill owners and those who sell to the mills think of this idea and accordingly request that they write their opinions to us. There are undoubtedly other reasons why the plan would be acceptable as well as why it would not. Inasmuch as the mill men, the dyers, the finishers, the chemists, the superintendents, etc., will also be affected we shall also value their opinions. Let us hear from all.

● COLUMBIA TEXTILE COURSES

Registration for students in the Evening Textile Courses at Columbia University began on Wednesday, September 18th, in Room 301, School of Business. The instructors may be consulted there about the courses given, between 7 and 9 P. M. during registration. Classes begin September 26th.

A special opening night for all students and courses will be held on Wednesday, October 2nd, in the Lecture Hall of the School of Mines (Room 306), at 7:30 P. M., during which textile films will be shown. The new talkie film on rayon by the North American Rayon Corporation will be the feature of the evening. The general public and members of the trade are cordially invited. Films on cotton manufacture as well as silk will also be shown.

A new course in silks will be given this Fall for the first time by J. J. Reutlinger of Hatch & Reutlinger, consulting textile specialists of New York. This course will be given every Tuesday evening from 7:30 to 9:20 in Room 410 B, School of Mines.

Practical courses in cotton and rayon yarn and fabric manufacture as well as textile design are offered on other evenings. These courses have been given for over 15 years.

Further information can be obtained by writing to Columbia University.

● CONNECTICUT CHEMICALS

The evolution of chemistry and chemical processes, as developed in Connecticut, will be an important feature of the Tercentenary Industrial Exposition which will be held at the State Armory, Hartford, from October 2 to 12. This exhibit of manufacturing process and products will have an entire display devoted to chemistry as it has affected industry in the past and aids it now.

Chemistry has made possible many diverse products, and Connecticut's chemical plants have likewise made many different commodities. Potash, an important product of the American colonies, was manufactured by Samuel Willard and others after experiments which lasted from 1735 to 1741. This was probably the first factory of its kind in New England. In 1794 a Scotch Company erected potash works at Suffield, and the founders brought apparatus with them. Powder for the Revolutionary armies was an important chemical product in early Connecticut, and it is thought that the first powder mill in the United States was first operated in the town of Glastonbury. A snuff mill was operated in East Hartford in 1784 and graphite was manufactured in 1813. An interesting invention was that of Dennison Olmsted of New Haven who, in 1827, was granted a patent for the manufacture of gas-light from cotton seed. The dye industry of the state was first given impetus by the making of silk dyes at a silk mill in Gurleyville.

● THROWSTER TINTS

The United States Testing Company, Hoboken, N. J., has a new line of Certified Throwster Tints ready for the trade. The line is composed of 40 distinctive tints for silk and 24 for rayon. Color cards and price lists will be sent to responsible concerns upon request.

The Testing Company is distributing an interesting leaflet on the instructions for the use of Certified Throwster Tints. Information is given for the proper preparation of tints and combination tints are listed for left and right twist yarns, including combinations for use under Cooper-Hewitt lights.

● GENERAL RELEASES

General Dyestuff Corp. announces release of bulletins on the following products. Copies are available upon request.

Chromoxane Brilliant Violet S B N—a new chrome color brought out by the I.G. and offered to the trade by General. When dyed from a Glauber's salt-sulfuric acid bath and aftertreated with bichromate it is said to produce bright violet shades of very good fastness to washing, fulling, potting, and decatizing. The fastness to light is said to be fairly good. It is further claimed that this dye is of good solubility and may be used for printing on wool, giving a good white discharge with Rongalite C. Beside its use as a self color, it is recommended by the manufacturers for brightening navy blue shades.

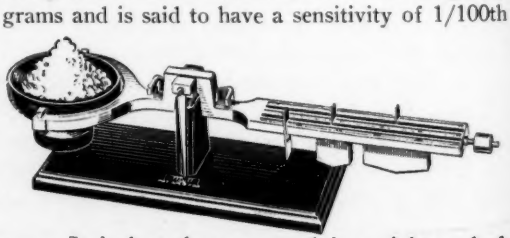
Diazo Brown 6 G A—a color which is said to produce with Developers ZA, A and MT, yellowish browns of good fastness to washing which are easily dischargeable.

● ABOPON

A new product called Abopon has been placed on the market by the Glyco Products Co., Inc., which is said to have many interesting properties for coating and sizing purposes for textiles, paper and leather. It is said to be a water soluble "resin" which will effectively displace alkalies in dissolving shellac and casein thereby giving solutions which are free from alkali. It is also claimed that solution can be effected at temperatures much lower than when alkali is used. It is further stated that in the case of shellac, the shellac wax remains in dispersion and does not rise to the surface in the form of a scum as when alkalies are used. Complete information may be obtained from the manufacturers named above.

● BENNETT BALANCE

The Chemical Publishing Co. announces production of the low priced Bennett Balance which will weigh up to 100 grams and is said to have a sensitivity of 1/100th of



a gram. It is less than a pound in weight and about twelve inches long and thus may easily be carried from place to place. It has an alloy steel knife edge and a highly polished agate bearing.

Textiles and the Newer

Synthetic Organic Chemicals

By B. A. HAROLD

DEFINITE strides in the field of synthetic chemistry have resulted in the development of numerous new commercial products. The unusual properties of some of these have opened possibilities for their use in conjunction with textiles. We refer to the development of synthetic rubbers as well as synthetic resins.

These compounds are somewhat still in their infant stages of practical applications; consequently their uses with textiles are still limited. There have been many individual resins developed, the chemistry of which is more intricate than those usually contacted by the textile industry. The writer will attempt in the following to describe some of these from the angle of general groupings with their properties, in that this simplification may disclose their possible uses with textiles. Practical textile applications of some of the newer synthetic organic chemicals will be discussed as well.

Although that which follows includes descriptions of compounds and products not often contacted in the field of textile construction and finishing, we hope that their strangeness will be overlooked in that they are being presented as possible adjuncts to be considered by the textile manufacturer. The unusual properties of some of these compounds, if added to those of certain textiles, may yield products offering commercial possibilities.

SYNTHETIC RUBBERS

The most widely known and used synthetic rubber at the present date is Duprene. This is formed by the action of hydrochloric acid upon monovinylacetylene, producing chloroprene which polymerizes to a rubber-like material.

Another product, Thiokol, although often called a synthetic rubber, is really a rubber substitute. This is a polyethylene sulfide formed by the inter-action between ethylene dichloride and an alkali polysulfide.

Koroseal is another rubber substitute, but will not be considered here in that the writer has only seen it commercially in sheet form and not as a liquid.

Duprene films when deposited upon a fabric or when impregnated into any porous material possess:

(1) Excellent resistance to animal, vegetable and mineral oils,

(2) A high degree of impermeability to gases,

(3) But slight tendency to absorb moisture,

(4) A high degree of resistance to the deteriorating influences of heat, light and oxygen of the air.

Duprene is marketed in latex form much akin to ordinary rubber latex, being made by emulsifying chloroprene and then allowing the latter to polymerize. The polymerized chloroprene of 45 per cent concentration is emulsified further with an ammoniacal sodium oleate soap solution. One part of this latex is diluted with one part of water in preparing an impregnating bath. Much in the same manner as impregnating rubber latex into a fabric, the fabric to be treated with the Duprene latex should be first thoroughly wet out in a one-quarter per cent solution of a wetting agent, as well as adding a small portion of the latter to the latex bath.

The greatest disadvantage of Duprene latex when used in conjunction with cotton textiles is that when a Duprene film dries and commences to age, there is an evolution of hydrogen chloride gas. This tends to tender the fabric. The action of sunlight activates the formation of hydrogen chloride. To overcome this effect the addition of 5 per cent of a carbon black dispersion to the Duprene latex is recommended. The carbon black tends to absorb the sunlight, counteracting its effect upon the Duprene. To further enhance the resistivity of the Duprene film to sunlight the impregnated fabric may be coated with a Duprene latex-carbon black-clay dispersion thickened with a casein solution.

Laboratory Report No. 162 of the Dupont Company states that fabrics coated with black Duprene latex compounds after exposure out-of-doors for two years showed little deterioration of the fabric.

Natural rubber latex may be added to Duprene latex to lend greater flexibility to the latter up to 20 per cent without materially affecting the resistivity of the subsequent film.

Thiokol is mostly available in liquid form as a cement, i.e., dissolved in organic solvents. The writer has seen and worked with aqueous dispersions of Thiokol. The films produced with this compound are very flexible and rubber-like, being unattacked by gasoline or oils. The great disadvantage in the use of Thiokol is that very obnoxious smelling and somewhat poisonous gases are produced when it vulcanizes.

SYNTHETIC RESINS

The use of resins in the finishing of textiles has been heretofore limited to the use of natural rosin soaps in kier-

boiling and as a binder for mineral fillers used in back-filling cloths. The details as to the preparation of a rosin soap has been described by Clark. (AMERICAN DYESTUFF REPORTER *23*, 571, 1934.)

The development of and uses for synthetic resins in the last ten years have been phenomenal. The exploitation of these resins directly into the textile field has been hampered because other industries have been created in their use. Thus, instead of bringing the resins to textiles, textiles have become a base material upon which to apply the resins. A second factor for the non-introduction of synthetic resins to textile manufacturers is that cloth-resin combinations require special machinery for their production. In the developments of these resins as well, water-soluble types which are a requisite in the textile industry have not been as numerous as compared to those soluble only in organic solvents.

There have been hundreds of various modifications of synthetic resins produced, but the more important ones may be grouped as follows:

(a) Phenol and urea—formaldehyde resins.
(b) Vinyl resins.
(c) Glyptal resins.
(d) Acetylene derivative resins.

We will give but a cursory description of these in that they have been described in detail by Ellis. (Ind. and Eng. Chem. *26*, 37, 1934.)

Phenol Formaldehyde and Urea-Formaldehyde Resins

There are hundreds of types of these resins present on the market today. They are produced by the interaction of phenol or urea with formaldehyde. Films produced with the urea base possess greater flexibility than the phenol type. Haveg which has been strongly advertised for the manufacture of dye kettles is prepared from a phenol-formaldehyde resin. In that these resins are unaffected by higher temperatures as well as by moderate concentrations of acid, they make ideal dyeing containers.

Vinyl Resins

These are produced by the polymerization combinations of vinyl chloride and vinyl acetate. Higher temperatures tend to soften this group of resins. They are used extensively for denture purposes. One of the vinyl group, polystyrene, possesses the highest insulating properties of any synthetic resin produced heretofore.

Glyptal Resins

These are prepared by polymerizing polyhydric alcohol and polybasic acid combinations. Films produced from these resins feature permanent flexibility.

Acetylene Derivative Resins

Duprene is a member of this group. Divinylacetylene known commercially as SDO (synthetic dyeing oil) produces a film possessing unusual acid resistance.

Synthetic resins have been prepared as well from petroleum derivatives treated with aluminum chloride. A resin highly resistant to chemical corrosion is manufactured by chlorinating rubber with tin chloride.

RESIN-TEXTILE COMMERCIAL DEVELOPMENTS

One of the more important attempts to utilize a synthetic resin as a coating for a textile was to produce waterproof adhesive plasters and surgical dressings. A drawback to adhesive plasters before the introduction of these resins, had been the loss of their adhesive qualities upon wetting. The excellent water resistance of certain of the more flexible phenol-formaldehyde resins overcame this.

The outgrowth of the above experimentation resulted in the marketing of a resin treated waterproof fabric called Revolite. In this process a cotton fabric is subjected to a calendering with a phenol-formaldehyde resinoid in such a manner that very minute penetration of the fabric occurs.

English Patent 387,125 describes the preparation of this semi-rubbery phenolic compound as follows: "Tung oil is reacted with a phenol-like resorcinol, in the presence of a metallic salt-like iron chloride, an organic salt like oxalic acid, plus a natural resin like rosin. This reaction is carried to completion with formaldehyde. Inert fillers such as starch, barytes, or wood flour may be added to the batch. Milling is carried out first on hot rolls and finished on cold rolls."

The Revolite cloth unlike rubberized cloth does not become tacky and possesses better aging properties than the latter.

The discovery of non-crease cellulosic fabrics has been made possible through the application of synthetic resins.

In the development of this process by Foulds, Marsh, and Wood (U. S. Patent 1,734,516, Nov., 1929) caution had to be exercised in the choice of resin solutions according to the nature of the material to be treated. Thus, solutions containing free phenol dissolved cellulose acetate,—other resin solutions destroyed hemp and jute. Substantial quantities of strong acid were undesirable for cotton fabrics, while permissive for wool.

The initial procedure for effecting a non-crease cotton fabric as described in the above patent is to first mercerize the material in order to thoroughly swell the fibers for maximum reception of the resin. The excess soda is then washed from the goods.

The resin solution is prepared by refluxing a mixture of 100 parts phenol, 100 parts 40 per cent formaldehyde, and 4 parts potassium carbonate for five minutes.

The mercerized cloth is passed through the resin bath and thence through a mangle, the nip being so adjusted that there remains 100 per cent pickup of the resin solution in the fabric. Drying is carried out on a tenter dryer, following which the goods are passed over drying cans at 170° C. for two minutes to effect polymerization of the resin. The fabric is then soaped to remove the excess resin, rinsed and then dried again.

The theory of this process is as follows: The most important aim is to penetrate the resin between the

micelles of the fiber rather than between the threads. The latter condition produces a harsh feeling fabric.

In the refluxing of the resin solution, the initial condensation product is formed and dispersed throughout the reaction mixture in the form of an emulsion. The presence of an excess of water in the fabric tends to keep the particles in a high state of dispersion. In the initial drying on the tenter frame, coalescence or coagulation of the dispersed particles occurs, whereby an irreversible colloid is formed. This may be termed the "gum" intermediate product. Further heating at a high temperature (170° C.) on the drying cans completes the reaction with the polymerization of the resin. We see that in the many stages of the resin formation there occur many colloidal phenomena.

If urea is substituted for the phenol in the above described process and the refluxed solution made acid with acetic acid, more flexible films are produced within the fabric.

According to Clayton (Jour. Soc. Dyers & Colorists *48*, 295, 1932) the advantages of resin treated cellulose fabrics are as follows:

(1) The fabric is nearer to a woven or knitted fabric of wool or silk in resistance to creasing as well as draping qualities.
(2) The dry strength and also the wet strength of rayons are increased.
(3) The weight of the material is increased approximately 15 per cent.
(4) Laundry shrinkage is reduced.
(5) There is a tendency to overcome the well-known slippage of rayon threads in which the filling tends to slip over the warp when the fabric is extended. Consequently many forms of distortion to which fabrics of this type are subjected are less liable to occur.
(6) There is a greater possibility of producing more satisfactory viscose-silk fabrics of the voile type with less susceptibility to damage in laundering.

While discussing the subject of non-crease cotton fabrics, it is of interest to note the very recent patent taken out by Gibbons (U. S. Patent 1,980,676) in which the effect is produced with a size-latex curable compound instead of with a synthetic resin.

In this process the cotton goods are first boiled out to remove pectin and coloring matters. A sizing bath is then prepared consisting of:

1 lb. casein
15 gal. water
2 oz. tri-sodium phosphate
5 gal. normal latex
2% dry sulfur (based on weight of dry rubber)
2% zinc oxide (based on weight of dry rubber)
2% accelerator (based on weight of dry rubber)

The opened goods are then run through this bath in open width and then mangled. The goods are run into a tenter dryer and worked in such a way as to prevent adhesion between crossed threads at the region of their overlap. Following the drying the goods are passed through a boiling soap solution which removes excess sizing. The final drying is executed without working the fabric. This process has found its major application for fabrics such as violes, piques, and organdies.

A most recent chemical development which has found a place for itself in textile processing and which has created large commercial outlets for its application is that of the use of special solvents for bonding fabrics containing cellulose acetate to produce "fused collar" fabrics. These fabrics are such that they are unaffected by moisture or perspiration, and shirt collars made from them retain their stiffness permanently.

Before this development, the main drawback to laminated fabrics was that the material used as a bonding agent was usually non-porous in itself; consequently the finished fabric was backed or lined with a solid, impermeable substance. The problem was to find a suitable bonding agent which was not only porous itself, but would remain so when processed.

In the new process described in the June, 1935, edition of Ind. and Eng. Chemistry, a fabric is prepared containing a mixture of cotton or linen and Celanese. The latter thread, after processing, serves as the bond to another external cloth.

With the development of synthetic rubbers and resins, one may wonder as to their effect upon the consumption of natural rubber latex for textiles. This should be little affected in that the synthetic compounds are in a much higher price range; and, secondly, due to their infancy much has yet to be learned regarding their adaptability to present methods of finishing textiles.

The production of synthetic rubber latices at the present writing involves comparatively small quantities. Due to this condition the price, for example, of Duprene latex is over eight times that of natural rubber latex. It should be some time before synthetic rubber latex supplants natural latex in practical usages.

Combinations of natural rubber latex with Duprene latex can be made in which the cost of the latter is reduced appreciably without influencing the chemical resistance of its films.

The chief advantage for which synthetic rubbers are sought is in their resistance to oils and solvents. The resistance of natural rubber latex films may be enhanced by the incorporation of proteinous substances like caseins or glues into the latex compounds. A compound of this type which will vulcanize with the heat of drying cans or in the average textile dryer is described as follows:

Latex (50% concentration)	1 gal.
Casein	12 oz.
Water	1 qt.
Zinc Oxide	1½ oz.
Sulfur	⅝ oz.
Accelerator No. 552	½ oz.
Agerite White Powder (anti-oxidant)	⅝ oz.

It is interesting to note that certain of the water-solu-

ble thermo-setting phenol-formaldehyde type resins may be added directly to a rubber latex bath to impart greater chemical resistance to the rubber. The writer has experimented with mixtures of this nature which have produced rubber films possessing better resistance to oils and solvents, though the films were not as flexible as those of the natural latex. The principle here involved is that upon application of heat the latex compound vulcanizes and the resin polymerizes simultaneously.

The fabric containing the cellulose acetate is treated with a mixture of solvents in which a partial softening of the Celanese occurs. While the fibers are in this plastic stage, heat and pressure are applied, by which they are anchored to the external fabric, forming a firm intersticed bond. In that the bonding occurs only at regularly spaced intervals, although close together, the permeability of the resultant fabric is maintained.

In this process the degree of permeability as well as stiffness imparted by the bonding is dependent upon the number of Celanese threads contained in a given area as well as upon the type of solvents used. Thus the more active solvents produce greater softening of the fibers and hence a firmer bond.

The shirt industry has found much use for this type of bonded fabric for collar material, one hundred thousand dozen shirts having been made with the "fused collars" in 1934, and it is expected that two million dozen shirts will carry this type of collar in 1935. It is anticipated that this process will be adapted in the textile field for palm beach suits, white uniforms, draperies, tapestries, and rugs.

Fabrics treated with synthetic resins have found wide use as noiseless gears requiring no lubricant, as well as for laminated sheets and tubes for use as acid resisting conveyors or media in the chemical industry.

As mentioned previously the greatest consumption of textiles today in conjunction with the newer synthetic products has been by the individual organizations producing these compounds rather than by the producers of textiles.

The development of pyroxylin-treated fabrics as leather substitutes has opened up a widespread field.

The use of synthetic organic chemicals, especially synthetic resins, still hold many possibilities for the textile industry, in printing and in finishing. They should be of material aid in producing the type of fabrics in which the present-day markets show interest, namely: (1) those possessing low water absorbing properties; (2) those which are fire-proof, and (3) those fabrics which are little affected when exposed continuously to abnormal conditions of light and air while still retaining their flexibility and elastic properties.

Wool Substitutes (Rayon)*

THE effect on wool industry of an increasing production of so-called wool substitutes, is the subject of keen controversy in Australia. It arises mainly from the big efforts made in Germany during the past twelve months to increase the production and use of artificial fibers with a view to bringing about a corresponding reduction in the quantity of wool imported. It is mainly from the wool point of view that the Australians are perturbed. As a matter of fact the Germans are equally concerned about reducing the imports of cotton and a considerable part of the artificial yarn produced competes with cotton more than with wool. It is significant, however, that Germany's imports of wool are increasing and would increase more rapidly if ways and means of paying for more wool could be devised. By national propaganda, and by dictatorial legislation, Germany may increase the use of clothing made from artificial fibers within her own country but that sort of thing cuts no ice outside Germany. In order to maintain her very essential export trade Germany must have wool—and the best merino wool, too. Hence her substantial purchases in South Africa and her negotiations in Australia for a reciprocal trade agreement. Apart altogether from the peculiar conditions arising from Germany's financial troubles, there is a perfectly natural development in the production of synthetic materials which can be used in conjunction with wool, cotton, silk and other natural fibers. It is only what one may expect in view of the progress in scientific research in recent years. Further striking developments may be expected in the future. One need only compare the earliest productions of artificial silk with the wonderful rayon fabrics of today in order to realize what can be accomplished.

Such names as "vistra," "wollstra" and "zellwolle" are now in common use in Germany, and, according to the latest reports, important changes have taken place which will have the effect of cheapening these various productions. The producers of the newer artificial fibers were given a considerable measure of protection in the form of minimum selling prices, but now there is to be a free market and producers will have to sell on ordinary competitive terms. Lower prices to the consumer will be the result and this should naturally result in an increased consumption. Both cotton and wool will be affected. But there is no need for Australian wool growers to be alarmed. The world demand for wool is keeping pace with the increase in world production and it is impossible to estimate the extent of the probable increase in the demand for wool goods in the Far East, especially in China. Enormous strides have been made in the United Kingdom in the manufacture of fabrics made from artificially-produced fibers, but there has been no falling off in the consumption of wool. In fact, the tendency is for wool consumption to increase. Price is, of course, a big factor and so long as wool is obtainable on a reasonable basis there will be an adequate market for it. The danger would come if wool rose to a price which would compel manufacturers to resort to the use of substitutes.

*Textile Mercury.

Dyeing and Block-Printing

in the Indian Bazaars*

Chequered History of Indigo

By "TRAVELLER"

THE Indians have been skilled dyers and printers for as long as history extends and to this day dyeing and printing as carried on in Indian bazaars provides many an arresting picture in spite of the advance of industrialism with its factories and its more prosaic methods of working. The alleys and back streets which make up the dyeing and printing quarters suggest a carnival, colored fabrics fluttering from balcony and upper window. Even the footpath provides its quota of color when youths are using it as a drying ground for brightly-colored silks. When this operation is in progress pedestrians meekly leave the footway and use the road, for custom is accepted in India. A middle room is usually the hanging chamber, particularly for the development of aniline blacks, and for drying goods during the monsoon rains.

Workshops Line the Street

Printers usually have their workshops lining the street so that intending purchasers—Mohammedan or Hindu women—can give orders to the printers to print a sari, and choose their design while he continues his work. At the rear, the dyer may be seen applying seductive colors to yarn and cloth in copper cauldrons, heated over wood fires. Such scenes provide rare settings for the artist, being rich in strong light and shadow, picturesque figures and intense color.

It requires a considerable effort of the imagination to visualize anything picturesque in a modern dyeing plant, with its coal-stacks and refuse heaps, its filter tanks and towering walls. Yet dyed fabrics of marvellous beauty, beyond anything imagined by the ancient dyer, are brought into existence amid these grim surroundings. Nor does the modern dyer find any romance in his craft, rather does the superb material passing through his hands become to him a daily worry; moreover, these days he has to share honors with the chemist and the engineer.

Indigo

One of the most famous Indian dyes is, of course, indigo. Its application is by no means a simple process, yet it has been mastered by dyers the world over, the ancient craftsmen bringing about reduction by indigenous substances. Africans used limy earths, crudely-made soda ash and sugary substances; one old Indian method embodied the use of lime dust, plantain (banana) ash, and a solution of certain seeds.

Perhaps no dyestuff has caused more trouble from a religious and political point of view, than indigo. Its introduction into Europe was bitterly opposed by growers of woad. In India, the dye was held in abomination by strict Mohammedans and high-caste Hindus. Mohammedans were prohibited from wearing indigo because it rubbed and stained, and no follower of the Prophet was allowed to wear such colors as were fugitive, when offering prayers within the mosque, and the same prohibition against the use of fugitive colors applied to prayer-mats used in the mosque. Likewise Brahmins were punished for wearing indigo, as it was considered abominable and the ground on which it was grown was impure for many years.

Before the introduction of synthetic dyestuffs into India, the dyer had to make use of the abundance of natural substances at his hand and many of these are still used in the old way, especially in the native States. There was a good choice of dye-producing material in the dense Indian forests—woods, barks, seeds, leaves, roots, flowers, but many of these required special preparation before they could be applied. The mordanting value of tannin-producing substances, was understood, and this often formed a preliminary treatment in dyeing. Mordanting by some tannin material followed by treatment with alum and oil were processes in the production of reds and reddish shades. Crude copperas—made by exposing iron pyrites to air and water—was used largely in the production of blacks.

Indigenous Products

Some of the indigenous products used by Indian dyers, were and are, in some cases, the following: indigo; cutch (*Acacia catechu*), catechu being made from the heart wood; turmeric, roots of the *Circuma longa;* the red flowers of the dhak tree; (*Butea frondosa*), yielding a yellow; aronotto (*Bixa orellana*) also yielding a yellow, which has been used to color butter and cheese in England, while American Indians used it to cover their bodies when in full dress; Dhao flowers (*Woodfordia floribunda*), used by silk dyers for dyeing red, these scarlet flowers growing in profusion all over India; Lodh, the ash of the *Symplocos racemoso,* which, along with turmeric and myrobalans (*Terminalia chebula*) was used for producing a fast red; Sandal wood (*Pterocarpus santalinns*) also giving a red; Indian mulberry (*Morinda elliptica* and *Morinda tinctoria*).

*Reprinted from "Dyer & Textile Printer."

When in India I paid many visits to the bazaar printing and dyeing establishments, and always found it interesting to watch the men at work. Generally the employees were on piece work, and labored when they felt that way inclined. On the whole, they were very expert craftsmen and a good deal of work would pass through their fingers when it was required.

Late one night as I was driving through the bazaar to my bungalow in Bombay, I passed a block-printer's workshop where the men were still at work, printing flimsy saris by the light of a flickering lamp. Although the air was sultry, they probably felt midnight to be pleasanter than the heat of the day—for it was during the hot season.

In some respects these craftsmen were to be envied. They struck me as never being in a splutter or worried; they worked when they wished, and rested when the fancy struck them, earning sufficient to supply their simple wants and pursuing a craft in which they took a real interest.

Friendly Craftsmen

I was in charge of a bleaching and dyeing works in Bombay at the time, and as I was interested in native handicrafts I often make excursions into the bazaars in search of something new, and rarely did I make a journey in vain. These craftsmen were very friendly when they became aware that we had something in common, and would often invite me into their small shops and send a boy out into the bazaar and bring me tea. The shops generally consisted of one room alongside the street, but about two feet above the street level, to be out of the reach of monsoon floods, for it was not unusual for eight to ten inches of rain to fall in a night, and, as often happens with the first burst of the monsoon, the drains are partially blocked up and the lower parts of the bazaar becomes a Venice in miniature. This is more particularly the case when the tide is up, and the exits to the sea are not free.

The typical Mohammedan printer as I knew him was a patriarchal character, with wrinkled face and long beard, kindly but terribly stubborn. On Fridays these old men looked very clean and smart, in white coats and wide trousers, on their way to the mosque for prayers.

Block Printing

On one of my evening rambles in the bazaar, next to a recess jammed between two buildings where a native was making lac bangles, I came upon a place, half dwelling-house, half block-printing shop, where men were hard at work printing a very cheap quality of sari cloth. The fabric had been dyed yellow, with a six-inch border of red produced by dipping. One man was printing a spot design in black, another blocking in red, and a third applying a black cover pattern. By the dim light of the street lamp they saw me watching them, and after the customary salutations the head printer offered me a *biddie* (native cigarette), and a few minutes later I was sitting inside the room drinking tea. The night was hot, and the half-dozen printers were semi-naked, an unusual proceeding for Mohammedans, who do not discard their coats with the same freedom as Hindus. The cloth for printing lay in piles alongside the various blocking tables, and the printers would draw the cloth as required, without changing their position. The printing-blocks shown to me were of blackwood, the sprig and spot designs in brass wire, but the stripes and blotches left in relief. Behind the blocking room was the hanging-room, where women dressed in red saris were assisting. These groups of figures—partly in gloom and partly in light—made a picturesque scene.

Block-Printing Outfit

At another establishment I was interested in a simple but efficient block-printing outfit. The color-box was made up as follows: Within a box 15 by 12 by 3 inches, was fitted a second box with a bottom of rubbered oil-cloth, which made a resilient but waterproof cushion, floating upon a thin layer of gum or discarded printing color placed in the bottom of the first box. When preparing for printing, the second box was fitted with a pad of flannel on which the printing color was spread, and on to which the printer dipped his block. Each application of the block to the cloth was followed by a tap with the closed fist. This constant tapping causes a hoof to grow on the side of the hand and by this a block-printer can always be recognized.

Steaming Prints

At the same place I was shown their steaming arrangement for prints. It consisted of an iron cylinder about a yard high, into which a little water was placed. Goods for steaming were placed within, protected from water splashes, and the lid closed. Then a charcoal fire was lit below, and the steam evolved fixed the colors. A style of printing carried out here was the printing of metals. A gum thickening was used which hardened after a few hours' exposure.

A Mohammedan acquaintance once invited me to see his block-printing shop at a quarter in Bombay known as Pydownie. The printers seemed a free and easy lot when I called upon them—one smoking, another resting. They were engaged in printing zinc dust—white and colored discharges—on dyed silk handkerchiefs. Several of the designs were quite intricate and the discharging was remarkably good, considering that the steaming arrangements were by no means under control. The cylinder, in which the goods were steamed, was similar to the one already described, being four feet by two. A little water was placed inside, a wood fire kindled beneath and the goods placed inside and left for several hours. There are a number of dyeing and printing businesses in this locality, but the styles do not vary greatly. They are mostly engaged in printing saris such as are worn by the merchant class of Hindu women.

Aniline black is printed extensively in the bazaars. In one place where I saw it being used the proprietor informed me that he had printed it for fifteen years. The black was developed by hanging, but the goods were not washed off. Tendering and smouldering of aniline blacks by heat developing is not unknown in the bazaar.

Printing Variations

As far as fastness and washing off of prints is concerned, there is a difference between printer and printer. Regularly printers passed my bungalow with bundles of prints on their heads, on their way to the sea, half a mile distant, where the goods would be washed off. Sea-water was free and there was no stint, whereas municipal water was scarce and dear. Some fortunate printers and dyers had a well in their back premises, and this simplified matters.

The following method of producing aniline black prints on cream grounds was communicated to me in Bombay. The pieces are taken direct from the loom and steeped in water overnight. Next morning workmen tread them with their feet, then wash them well and dry them in the sun. The black printing color is made from aniline salts, tartaric acid and copper sulfate. The prints are exposed to the sun until the black is developed. They are then washed by stamping with the feet, dried, and tinted in a bath containing chrysophenine. Next they are passed into a fresh bath containing yellow earth (iron oxide). A little is added at a time, and stamped in with the feet, the goods being lifted between each addition. The dyer then runs his hand along the selvedge, another workman takes hold, and the piece is squeezed and dried quickly in the sun. It is a simple process for which the dyer got four pence per piece. If red was wanted, magenta was printed.

Prices for dyeing and block-printing vary considerably, and there is no uniformity in conditions. The same variations likewise occur in the quality of the work, not so much in the application as in the nature of the after-treatment and in the dyes used. According to one price among my notes, the Ahmedabad block-printers were paid two annas (two pence) for printing a large sized sari. In Bombay, a printer informed me that they could print 100 25-yard pieces a day, and the profit on a sari length was one pice (a farthing).

Wherever one moves in Indian bazaars, one is sure to come into contact with interesting side-lines in connection with this craft. It may be a woman sitting behind her tray of sweetmeats on the edge of the pavement, knotting a garment for tie-dyeing as she waits for customers. Or perhaps one will see a bundle of cloth tied up tightly at the ends ready for dipping. When wandering through the dyeing quarter of one bazaar, I came across a most interesting example of tie-dyeing, half-finished. It was a bunch of muslin tied in thousands of knots, and portions of the cloth had been dipped in several colors, and re-tied. It was awaiting another dipping. I bought the cloth as it was, and have it still. I found later that the muslin was not of one thickness, but of several, so that when finished it would have be unwrapped to a considerable length. The price I paid for it was just a few rupees.

A Native Dyer's Triumph

It was at a small one-man dyeing establishment where I witnessed one of the greatest triumphs of the native dyer. His dyehouse was the size of a hen-cote, and he occupied the center of it, standing in a flat dish containing a sari and about a pint of dye-liquor, kneading the dye into the cloth with his feet. From time to time he would lift the sari, add a few more drops of dye, and continue the kneading operation. This dyer had practically four hands, and he used little more dye than would well wet the sari. For economy this man's methods would take some beating, and from the few dyed objects hanging about, I saw that he produced goods results.

Alizarine red is largely printed in all Indian bazaars. In fact, it is believed that Turkey red originated in India, and passed thence through Western Asia and Greece to Turkey.

A seventeenth century traveller stated that he saw Hindoos printing on to cloth, what we known as mordants—acetate of iron mixed with palm oil and rice water for black, and alum water mixed with sappan wood for red. The cloth was then exposed to the hottest sunshine, and afterwards well washed in water. The cloth was then dyed in certain woods, and the patterns came up black and red where the mordants were printed.

Block-Printing in Ahmedabad

A good deal of block-printing is still carried out in Ahmedabad, but only a fraction of what was done before printed Indian shirting arrived from Lancashire printworks, for this was the style on which they were mostly engaged. At the present time Ahmedabad is having its revenge on Lancashire by increasing its cotton factories. There is an old Indian proverb that the prosperity of Ahmedabad hangs on three threads—silk, gold and cotton. At present most of the weight is on one of them—cotton.

The Ahmedabad printers did not steam their red prints, but developed and fixed them on the sandy banks of the River Sabarmati. There the goods were spread, and the combined influences of damp, dew and sun both developed and fixed the red. I have seen the people—both men and women—engaged on this task, sprinkling the goods with water, and washing them in the river.

It was during my residence in Bombay that I met Mr. C. P. Baker and his son. Mr. Baker was at the time engaged on his monumental book on the history of block-printing in India, and had just returned from a tour round the Malabar coast, where much printing was carried on, and to Lucknow where printing was done in sprig patterns by a method similar to the old madder style, buffalo milk and castor oil being used in the mordanting process. Mr. Baker showed me some exquisite samples of prints which appeared to have been produced by indigo dipping over painted wax designs. One cloth showed the stamp of the East India Company.

Possibly a person interested in dyeing and printing who goes to India today will find that since I left it, not many years ago, some of the establishments I saw have disappeared and that old methods have been abandoned—particularly in the more populous centers. Nevertheless, I am given to understand that in many a place, especially in the Native States, the old coloring matters and the old ways still hold their own.

TECHNICAL NOTES FROM FOREIGN SOURCES

Vat Dyestuff

German Patent No. 500,177 (*June* 18, 1930)—*I. G. Farben-Ind. A.-G.*—1-2-2'-1'-Anthraquinone-azine can be prepared in a single operation according to the procedure of German Patent No. 498,292. According to the specification of the present patent, the product is treated with halogen halides, or compounds evolving them, in the presence of reasonably aqueous sulfuric acid. The reaction can be carried out in a single operation by use of halogen acid, with the procedure of the patent above referred to. A sulfuric acid of 50-75% works best. It is also convenient to use alkali halides, which with the sulfuric acid will liberate the halogen acid, instead of one's troubling with the free halogen acid.

For example, the 1-2-2'-1'-anthraquinone-azine is stirred up with 60% sulfuric acid, and into the suspension is dropped slowly a saturated solution of common salt. This is carried out at 95°-100° C., and afterward the mixture is stirred for two hours longer at the same temperature, then diluted, the dyestuff filtered off, and washed.

The product is a chlor-derivative of N-dihydro-1-2-2'-1'-anthraquinone-azine.

Vat Dyestuffs (Indigoid)

German Patent No. 499,745 (*June* 16, 1930)—*I. G. Farben-Ind. A.-G.*—The new point of the method protected in this patent consists in condensing thionaphthene or its derivatives with phthalic anhydride or its derivatives, in the presence of condensing agents, and then subjecting the thionaphthenoyl-o-benzoic acid formed to further condensation (closing of the ring).

For example, 20 parts of thionaphthene and 33 parts of phthalic anhydride, together with 25 parts of anhydrous aluminium chloride, are stirred up in carbon disulfide as an inert medium, and the mixture, after being stirred at the ordinary temperature for a day, is heated upon the water bath until the reaction is ended. It is then treated with ice and hydrochloric acid, the carbon disulfide distilled off, with steam, and the residual thionaphthenoyl-o-benzoic acid purified by dissolving it in sodium carbonate solution, filtering, boneblacking if necessary, and acidifying, the product being reprecipitated. Of this purified product, 5 parts are treated in the cold with so much thionyl chloride that complete solution takes place, and this solution gently warmed to complete the reaction (the chloride of the acid is formed, and HCl and SO_2 escape). The excess of thionyl chloride is then distilled off in vacuo, the residue, the acid chloride, dissolved in carbon disulfide, treated with 10 parts of anhydrous aluminium chloride, and heated under reflux on the water bath for some hours (ring-closing), then cooled, treated with ice and HCl, the carbon disulfide distilled off with steam as before, and the solid residue, the product, isolated; in this case, it is the already known phthaloyl-2-3-thionaphthene.

The product dyes wool yellow from a weakly alkaline hydrosulfite vat. The products obtained from the various substitution products and homologues of the fundamental intermediates may be used, as such, as vat dyestuffs, or subjected to further reactions which will lead to other vat dyestuffs.

Vat Dyestuffs (Anthraquinone Series)

German Patent No. 475,687 (*May* 3, 1929)—*I. G. Farben-Ind. A.-G.*—A patent with specifications carefully defined.

(a)—Ortho-amino-hydroxy-anthraquinones are condensed with anthraquinone-aldehydes, or substances which yield such aldehydes during the reaction, by heating in the presence or absence of solvents or media.

(b)—Anthraquinone-carboxyl - amino - anthraquinones, substituted in the ortho position to the amino-group by a hydroxyl or negative group, are subjected to endo-condensation in presence or absence of solvents or media, and in presence or absence of catalysts, etc.

(c)—Any other method which will yield an anthraquinone with one or more oxazole groupings, which are substituted in the mu-position by an anthraquinone radical.

In all the above, the anthraquinone radicals may contain any substituting groups as desired.

The products are stated to possess a striking affinity for vegetable fibers when vatted, and to vary greatly in color-tone according to the substituting groups in the anthraquinone radicals.

Two examples are given, describing among others a bright yellow and a very fast bluish-red.

Vat Dyestuffs (Benzanthrone Series)

German Patent No. 498,681 (*May* 24, 1930)—*I. G. Farben-Ind. A.-G.*—In the process described in this patent, 2-2'-dibenzanthronyls or their substitution products are treated with nitrating agents in excess, with or without solvents or dilutive media, and the products which may be purified, and reduced in certain cases if desired, also treated with alkylating agents, if so wished. The temperature of nitration is low. The crude products may be purified, e.g., by extraction with alkalies or alkaline sulfides, the use of the latter of course involving the reduction of nitro-groups which were introduced by the nitrating agent. The products apparently contain one or more hydroxyl groups beside the nitro or amino groups; and in some cases alkylation improves the properties of the products.

The one example of several, 2-2'-dibenzanthronyl, 90 parts, is added to 600 parts of nitric acid of 48° B. (a very great excess) with careful stirring, at a temperature of about 5° to 10° C. After 3 hours standing at ordinary temperature, the dark-red solution is diluted with water, and the yellow-olive precipitate filtered off and washed.

It is soluble in conc. sulfuric acid with a brown color: in dilute caustic alkalies its solution is brownish-violet (solubility is the evidence of hydroxyl groups, apparently); the hydrosulfite vat is dark violet, dyeing cotton gray.

Dyeing of Mixed Weaves Containing Rayons, Especially Vistra-Wool Mixtures

R. Huenlich—Monats. f. Seide u. Kunst-Seide 39, 337 (1934).—The trade's interest in mode-weaves is at present directed mostly toward mixed weaves, especially those containing viscose or Vistra. The characteristic aspect, consistency, and the suitability of the fabric for definite kinds of use, as well as the feel or scroop, are determined mostly by the nature of the raw stock, the twist of the yarn, the structural characteristics of the weave, and finally by the dyeing and finishing. Now viscose may quite correctly be considered as the most sensative material met with in dyeing, since its tensile strength, in the wet condition, is low compared with that of other fibers, and the same factor is also dependent, in the "dry" state, upon the moisture-content of the air. It does not matter much whether the titer is high or low; and, furthermore, over-stretched or completely stretched viscose differs from the normal grade not only in titer, but in luster also. If one exerts a certain tension upon a strand of viscose, the latter stretches, and does not go back to its original length when the tension is released, but contracts only partially. Its elasticity is therefore greater than its tensility. At higher degrees of humidity, each of these properties is of a higher value, and at a lower humidity, is less. Forcible extension alters the structure of the fiber, and likewise its affinity for dyestuffs. To assure even results in dyeing, care must be taken, in the spooling and other preparation, to insure a suitable and uniform tension upon the fiber, and also to maintain a fixed degree of humidity in the workrooms. Humidity-control devices cannot be to highly valued, especially during the warmer seasons of the year.

Oil spots, too, are a cause of much difficulty, since they can be removed from a weave only with the greatest difficulty, if the risk of alteration of the structure of the fiber at such areas is to be avoided. Saponifiable oils ought to be used in any parts of machinery from which oil can possibly get upon the weave. Sometimes, viscose yarn is oiled before or during spooling; again, such oils should be of a type easily saponifiable and easily washed out completely. The weaver should also inform the dyer in exact terms as to the nature of all fibers used in the weave leaving his hands.

That is, the dyer should be given clean goods properly woven, and definitely understood as to nature, if good work in dyeing is to be required from him—surely not an unreasonable thing to expect.

The remainder of the paper consists of a general, though exactly worded, description of the types of dyestuffs suitable for the weaves in question—both viscose and acetate silk are considered; but nothing which seems to warrant special quotation. The whole paper (so far—it is to be continued) is well written, and is a worth while resume.

Fast Chrome Dyestuffs in Printing Upon Wool

TIBA 11, 35 (1933). — A review of the progress achieved in the dyestuff industry during the past thirty years shows that there have been many attempts made to discover dyestuffs of good general fastness. These efforts have been successful in certain directions, and the Indanthrenes, the Indigosols, and the Naphthol AS series may be mentioned as not merely individual, but actual, group-achievements.

Cotton and its artificial representatives, as viscose, have responded to these discoveries, so to say, in a decided manner. The intrinsic value of these fibers has been increased in degree by the new possibilities of dyeing them in shades of a confessedly greater and greater fastness, and printing upon these fibers would hardly have attained its present level without the help of these new dyestuffs. But, in considering these advances in the art of dyeing vegetable fibers, we must admit that a parallel has not been established for the dyeing or printing of wool.

For wool, the use of the vat colors, the Indigosols, and the Naphthol AS methods has achieved only a moderate success, and has encountered difficulties of both a technical and an economic nature, although different attempts have been made, with the purpose of insuring, in this field, the same degree of success as has been attained with cotton. The dyeing of wool has never, as yet, undergone any fundamental modifications. The achievements of the dye-producer in this direction have consisted in the enrichment of the dyer's choice of colors by enlargement of the series of chrome dyestuffs, acid dyestuffs, and dyestuffs of a less acid nature.

Most of the woolen weaves found upon the market have been printed with basic colors. In spite of the great number, now available, of dyestuffs of good fastness, the dyer seems frequently to choose dyestuffs far from being suited to the kind of work for which they are chosen. The result is, that the dyeings are not solid dyeings, and the desire of the consumer for a more stable dyeing is really justified.

Now, it is undeniable that we sometimes find, among the printers, a "certain uncertainty" as to the choice of his dyestuffs. Sometimes the dyestuff used is so fast that it outlasts the fabric; sometimes so actually fugitive that it ruins the value of the weave; in other words, the printer goes from one extreme to the other. Those who believe that they can demand from printed woolen weaves the same degree of fastness of color as from printed cotton weaves are quite in the wrong, and lose sight of the difference in nature between the two fibers. For example, woolen muslin printed for dress goods must possess a good fastness toward light, perspiration, and ironing. Besides, it ought to stand up under a normal domestic laundering at 40°-50° C. in a bath of 5 g. of marseilles soap or 5 cc. of ammonia water per liter. These are special requirements for that particular type. If the choice of dyestuffs is thoughtfully made, we can find among the acid or sub acid dyestuffs products which will possess the quality desired.

For goods which demand a still higher degree of fastness, we find among the group of "fast chrome dyestuffs" colors which are suitable for very stringent demands. These colors are really "developed," either upon a chrome mordant, or by after-chroming, or by being subjected to chroming in substance, before isolation as solid products to be sent out into commerce; and have of recent years gained an important position in the dyeing of woolen weaves in the bath.

It is natural that a desire should have arisen, of employing these dyestuffs in the printing of woolen weaves also. The reason why such dyestuffs, up to now, have not found more than a kind of restrained employment in printing upon wool, may be that these products are not as familiar to chemists as one would suppose them to be, and perhaps, too, because the trade was formerly less insistent upon the fastness of prints upon wool than is now the case.

Now, compared to chrome dyestuffs used for printing upon cotton, and adapted equally for application to wool, the fastness of the dyeings toward washing and light of the modern, special chrome dyestuffs is distinctly superior. They attain a degree of fastness which can otherwise, with other dyestuffs, be equalled only by actual mordant printing.

In the printing of patterns upon wool, these chrome colors seem destined to fill a serious gap which has existed. In the series of acid dyestuffs, which are still commonly used for such work, there is lacking a bright blue which can be discharged to a permanent white; and every printer appreciates the vexation of seeing a white discharge-pattern gradually become bluish, in storage or in clothing in the act of being worn. The acid colors are not sufficiently fast, furthermore, to perspiration, washing, or ironing. In all these points, the chrome colors are distinctly superior.

Several detailed formulae for printing-pastes are given, with details of use.

Vat Dyestuffs

German Patent No. 499,352 (*June* 11, 1930—*I. G. Farben-Ind. A.-G.*—The process here protected consists, in general, in subjecting the vat dyestuffs of German Patent No. 212,471, or their derivatives, to destructive oxidation, almost any oxidizing agent, alkaline or acid, being quoted as suitable; in some cases, indeed, more than one oxidizing agent being employed. The reaction is made evident by the vigorous evolution of carbon dioxide, and apparently leads to complex derivatives of phenanthridone, the simplest product cited being apparently a diphthaloylphenanthridone, of an olive-yellow color.

In the same way, derivatives of the original substances whose substituent groups are attached either to a carbon or to a nitrogen atom, or which may be members of other isocyclic or heterocyclic series, as for example the products of German Patent No. 461,193, or of French Patent No. 640,939, may be similarly employed.

The products generally differ from the original substances in color; they mostly give a yellow to olive-yellow color when dissolved in conc. sulfuric acid; their vats are usually brown to violet.

Five examples in all are given—very varied.

Vat Dyestuffs (Pyrazol-anthrone Series)

German Patent No. 498,067 (*May* 30, 1930) (*addition to G. P. No.* 493,813 *of August* 10, 1928)—*I. G. Farben-Ind. A.-G.*—The principal patent covers the preparation of vat dyestuffs by condensing pyrazol-anthrone with 1-amino-2-halogeno-anthraquinones or their substitution-products, by treatment with alkaline condensing agents in the heat. The present supplement describes the condensation of 2-halogeno-pyrazol-anthrones with 1-amino-anthraquinones or their substitution products, again by means of alkaline condensing agents in the heat—i.e., a translocation of the reactive groups from one component to the other respectively. If an excessive amount of the amino-anthraquinone is used, a red vat dyestuff, already described in German Patent No. 454,425, or derivatives of it, is also formed, which is to be avoided as far as possible, in order to avoid complications in the purification of the desired product. In an example given, 2-brom-pyrazol anthrone, 11.6 parts, is mixed with 17.6 parts of 1-amino-anthraquinone, 7 parts of potassium carbonate, 0.4 part of copper powder, and 100 parts of nitrobenzene, and the mixture boiled, with constant stirring, as long as the quantity of dyestuff formed increases. Thereafter, when the mixture has cooled, the nitrobenzene is removed by distillation with steam, and the inorganic constituents of the residue removed (the carbonate and halide formed being in solution in the condensate in the still, and the copper, e.g., removed by dilute nitric acid); or the cooled mixture is merely diluted with alcohol, the crude product filtered off, washed with alcohol, and then with water. To remove unchanged amino-anthraquinone, the product is extracted with 70% sulfuric acid. The dyestuff may finally be purified by crystallization from boiling dichlorbenzene.

This product is very similar to the one described in example I of the original patent.

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